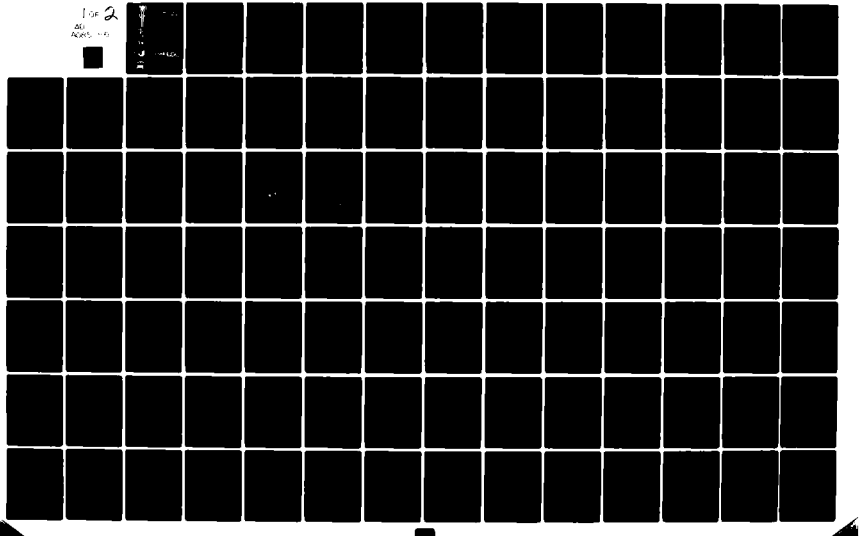
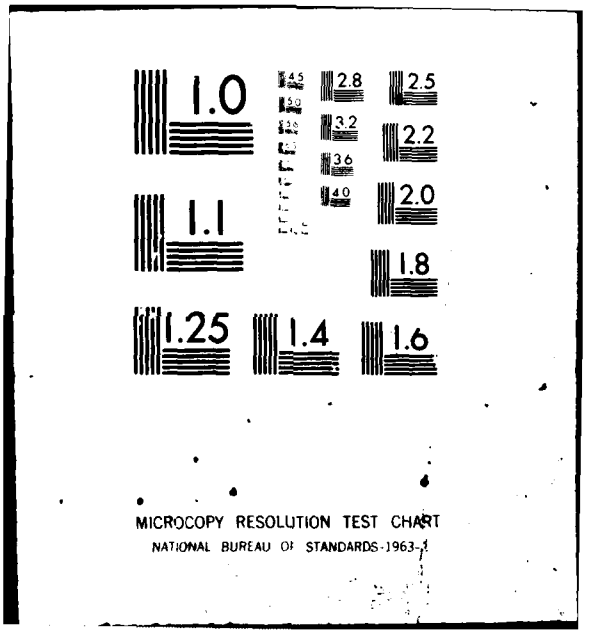
AD-A085 186 AIR FORCE ENGINEERING AND SERVICES CENTER TYNDALL AF--ETC F/G 21/9.1
THE EFFECTS OF AMINE 'BASED MISSILE FUELS ON THE ACTIVATED SLUDG--ETC(U)
OCT 79 M G MACNAUGHTON, J A FARMWALD
UNCLASSIFIED AFESC/ESL-TR-79-39 NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ESL-TR-79-39

THE EFFECTS OF AMINE BASED MISSILE FUELS ON THE ACTIVATED SLUDGE PROCESS

MICHAEL G. MACNAUGHTON
JAY A. FARMWALD
ENVIRONICS DIVISION
ENVIRONMENTAL SCIENCES BRANCH

OCTOBER 1979

FINAL REPORT
JUNE 1977 - JULY 1979

AFESC

ENGINEERING AND SERVICES LABORATORY
AIR FORCE ENGINEERING AND SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

NOTICE

Please do not request copies of this report from HQ AFESC/RD (Engineering and Services Laboratory). Additional copies may be purchased from:

National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

Federal Government agencies and their contractors registered with Defense Technical Information Center should direct requests for copies of this report to:

Defense Technical Information Center
Cameron Station
Alexandria, Virginia 22314

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: ESL-TR-79-39	2. GOVT ACCESSION NO.: AD-A085 786
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): THE EFFECTS OF AMINE BASED MISSILE FUELS ON THE ACTIVATED SLUDGE PROCESS	5. TYPE OF REPORT & PERIOD COVERED: FINAL REPORT Jun 77 - Jul 79
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Michael G. MacNaughton; Jay A. Farmwald	8. CONTRACT OR GRANT NUMBER(s): 107
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Sciences Branch, Environics Division; Air Force Engineering and Services Laboratory; Tyndall Air Force Base, Florida 32403	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: JON: 2103-7W-84; Program Element: 63723F; 7W
11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Engineering and Services Laboratory; Tyndall Air Force Base, Florida 32403	12. REPORT DATE: Oct 79
	13. NUMBER OF PAGES: 106
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): PE 63723F	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

AFESC/ESL-TR-79-39

18. SUPPLEMENTARY NOTES

Availability of this report is specified on verso of front cover.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrazine	Activated Sludge	Unsymmetricaldimethylhydrazine
Missile Propellants	Monomethylhydrazine	Toxicity
Biodegradation	Environmental Chemistry	
Environics	Pollution Control	
Environmental Quality	Amine Fuels	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Air Force (AF) procures amine based hydrazine fuels for use in Titan II and III, Minuteman III, Bomarc and F-16 systems and is also responsible for the procurement, storage, and transport of such fuels in support of the National Aeronautics and Space Administration (NASA) and the AF Space Shuttle Program.

This report summarizes data on the effects of Hydrazine (HZ), Monomethylhydrazine (MMH), and Unsymmetricaldimethylhydrazine (UDMH) in conventional →next page.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED 394633

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (Concluded) activated sludge systems for semi-continuous addition of waste containing the fuels and for slug doses from accidental spills.

It was concluded from the continuous feed studies that the three hydrazines could cause significant deterioration of an activated sludge plant if the concentration in the influent exceeded a few mg/ℓ. For an aeration basin with a common hydraulic detention time of 9 hours, the efficiency of organic removal is seriously degraded when the influent concentration of HZ exceeds 10 mg/ℓ. For UDMH and MMH this total failure results at concentrations of approximately 8 mg/ℓ and 5 mg/ℓ, respectively. Interpolating from these continuous feed studies, the "no effect level" would be approximately 1 mg/ℓ for HZ and 2 mg/ℓ for MMH and UDMH.

The influence of the hydrazines on nitrogen speciation of the sewage treatment plant effluent is more pronounced than that found for organic carbon oxidation. Inhibition of nitrification occurred at concentrations above 0.5 mg/ℓ for MMH and 1 mg/ℓ for the other fuels.

Only at the lowest HZ concentrations tested (<1 mg/ℓ) was the effluent fuel concentration below detection limits, and for MMH and UDMH the maximum removal efficiency observed was 89 percent and 96 percent, respectively. Other AF-sponsored studies on the effect of these fuels on algae have established "no effect" concentrations of less than 0.001 mg/ℓ for MMH and 1.56 mg/ℓ for UDMH.

For slug doses (because of the short exposure) the effect of transient high fuel concentrations would be less than for a continuous exposure. The concentrations found to cause no significant effect on sewage treatment efficiency are 74 mg/ℓ for UDMH, 44 mg/ℓ for HZ, and ∿32 mg/ℓ for MMH. Ammonia oxidation was effected for all three fuels at the lowest concentration tested (∿25 mg/ℓ). Recovery times for the highest concentrations tested (∿ 250 mg/ℓ) are in the range of 2 to 5 days.

Extensive background information is presented on the theory of dispersed growth bacterial systems.

PREFACE

This report summarizes work performed in accordance with Technical Need (TN) SAMSO-AFCEEDO-1302-76-49, "Disposal of Hydrazine Fuels Hazardous Waste," under program element 63723F, JON 21037W84. The project officers were Major Michael G. MacNaughton and Capt Jay A. Farmwald of the Civil and Environmental Engineering Development Office (CEEDO). Effective 1 March 1979, CEEDO was inactivated and became the Engineering and Services Laboratory (ESL), a directorate of the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403. This work was begun in June 1977 and was completed in July 1979.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public including foreign nations.

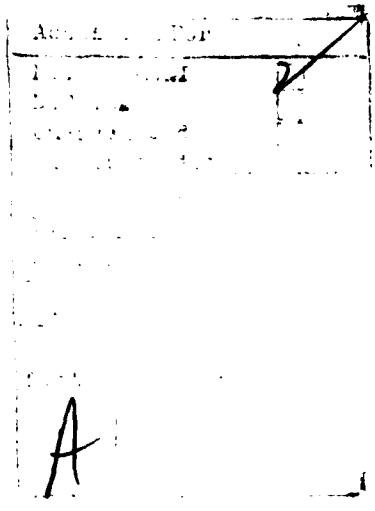
This technical report has been reviewed and is approved for publication.

MICHAEL G. MACNAUGHTON, Major,
USAF, BSC
Chief, Environmental Sciences Div

JAY A. FARMWALD, Capt, USAF, BSC
Environmental Engineer

EMIL C. FREIN, Lt Col, USAF
Chief, Environics Division

GEORGE D. BALLENTINE, LtCol, USAF
Director, Engineering and
Services Laboratory



(The reverse of this page is blank.)

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONCLUDED)

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONCLUDED)

LIST OF TABLES

LIST OF TABLES (CONCLUDED)

SECTION I

INTRODUCTION

1. BACKGROUND

The Air Force (AF) procures amine based hydrazine fuels for use in Titan II and III, Minuteman III, Bomarc and F-16 systems and is also responsible for the procurement, storage, and transport of such fuels in support of the National Aeronautics and Space Administration (NASA) and AF Space Shuttle Program. This results in an annual movement of approximately 2.36 kilograms (5.2 million pounds) of neat hydrazine (HZ), monomethylhydrazine (MMH), unsymmetricaldimethylhydrazine (UDMH), and Aerozine 50 (1:1 HZ:UDMH). Within private industry significant quantities of neat hydrazine are used as plastic blowing agents, anticorrosion agents for boiler waters, and growth inhibitors. MMH and UDMH are not widely used outside of NASA and the Department of Defense (DOD). The AF problem with respect to neat hydrazine is complicated by its use in the Emergency Power Unit (EPU) on the new F-16 aircraft which will be deployed worldwide. The EPU on the F-16 contains 24.6 liters (6.5 gallons) of a 70-percent aqueous hydrazine solution, and potential small spills during maintenance and handling of the unit require simple and effective cleanup procedures.

Documenting the ability of conventional biological waste treatment facilities to assimilate low concentration hydrazine wastes on a semi-continuous flow basis and/or slug loads resulting from transportation/operational spill situations would greatly simplify the development of preferred neutralization methodologies in single event scenarios. To evaluate the assimilative capacities of such domestic treatment systems, this research was developed to investigate both activated sludge and trickling filter unit processes. This report will summarize data on the effects of HZ, MMH, and UDMH in conventional activated sludge systems.

2. SCOPE

Using bench scale continuous flow recycle reactors a series of experiments were conducted to accomplish the following:

- Establish control parameters favoring the oxidation of both carbonaceous matter and ammonia (nitrification) for a supplemented primary effluent.

- Evaluate treatment efficiency under the selected operating conditions as a function of various continuous flow missile fuel concentrations.

- Document the effects of shock loadings under the selected conditions and monitor process recovery.

These data will serve as a basis for comparison with alternative physical/chemical treatment technologies in formulating AF contingency plans and should also prove useful in impact assessment exercises.

SECTION II

THEORY/BACKGROUND

1. DISPERSED GROWTH SYSTEMS

a. Substrate Utilization: The kinetics of soluble substrate utilization by dispersed bacterial populations are a function of the limiting substrate and microorganism concentrations. A relationship similar to that derived empirically by Monod (Reference 12) has been proposed for such systems (Reference 5).

$$\frac{ds}{dt} = \frac{kSX_a}{K_s+S} \qquad (1)$$

$\frac{ds}{dt}$ = Substrate utilization rate per unit volume (mass/volume - time).

k = Maximum rate of substrate utilization per unit weight of microorganisms - at high substrate concentrations (time $^{-1}$).

S = Limiting substrate concentration surrounding the microorganisms (mass/volume).

K_s = Half velocity coefficient (mass/volume).

X_a = Microorganism concentration (mass/volume).

Graphically, Equation (1) may be represented as shown in Figure 1. Inherent in this model is the assumption that only one substrate is limiting and that this substrate is both soluble and biodegradable.

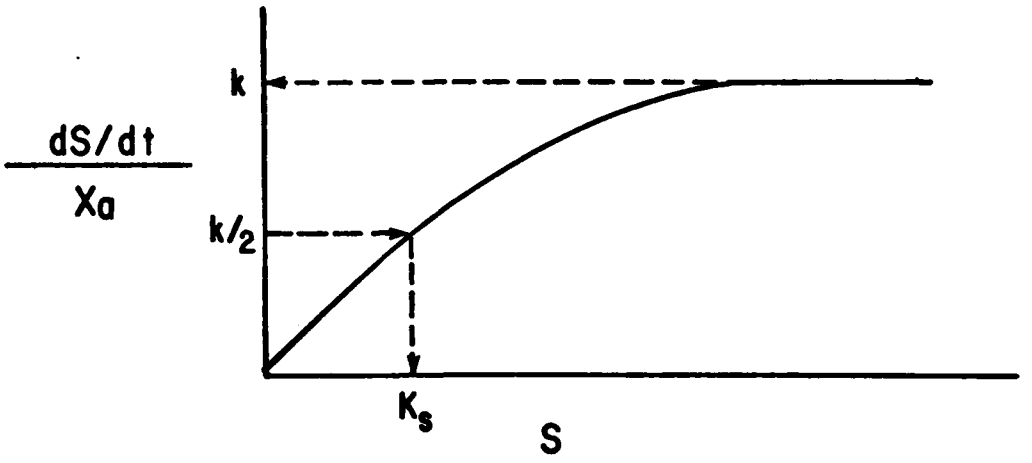


Figure 1. Specific Substrate Utilization as a Function of Substrate Concentration, Monod Plot

b. Bacterial Growth: The empirical equation for bacterial growth (Reference 13) is:

$$\frac{dX_a}{dt} = Y \frac{ds}{dt} - bx_a \qquad (2)$$

$\frac{dX_a}{dt}$ = net growth rate of microorganisms per unit volume (mass/volume-time).

Y = maximum yield coefficient (mass/mass).

b = microorganism decay coefficient (time $^{-1}$).

Equation (2) may be rearranged to:

$$\frac{dX_a/dt}{X_a} = Y \frac{ds/dt}{X_a} - b \qquad (3)$$

On a finite mass and time basis where M refers to a definite mass of microorganisms (Reference 4):

$$\frac{(\Delta X_a/\Delta t)_M}{(X_a)_M} = Y \frac{(\Delta S/\Delta t)_M}{(X_a)_M} - b \qquad (4)$$

c. Definitions: Using the above relationships, many useful parameters have been defined (References 4, 5).

(1) Net Specific Growth Rate: (μ)

$$\mu = \frac{(\Delta X_a/\Delta t)_M}{(X_a)_M} \qquad (5)$$

Substituting Equation (1) into (3) and using Equations (4) and (5) we may further show that:

$$\mu = \frac{YkS}{K_s+S} - b \qquad (6)$$

When b = o and $S>>K_s$ μ_{max} can be defined:

$$\mu_{max} = Yk \qquad (7)$$

(2) Mean Cell Residence Time: (Θ_c)

$$\Theta_c = \frac{1}{\mu} \qquad (8)$$

Equations (5) and (8) result in Equation (9).

$$\Theta_c = \frac{(X_a)_M}{(\Delta X_a/\Delta t)_M} \qquad (9)$$

(3) Specific Utilization: (U)

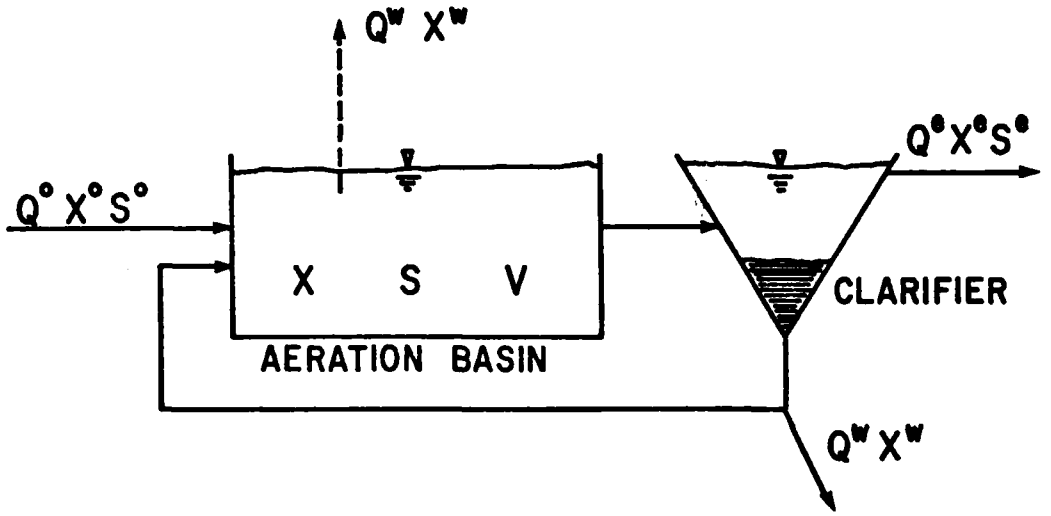
$$U = \frac{(\Delta S/\Delta t)_M}{(X_a)_M} \qquad (10)$$

d. Complete Mix - Cellular Recycle :

Figure 2 illustrates this classical treatment system which employs solids (cellular) recirculation in order to make Θ_c independent of the hydraulic detention time (Θ). However, as pointed out by Lawrence (Reference 5), Θ_c cannot be varied completely independent of Θ due to the practical limitations imposed by the settling characteristics of the biomass.

In developing relationships for complete mix recycle systems, several assumptions apply:

- Waste stabilization occurs only in the aeration basin (conservative assumption).
- Instantaneous and complete mixing occurs in the aeration basin.
- The total active biological mass in the system is equal to the biological mass in the aeration basin, i.e., the clarifier simply serves as a source of biomass through constant and continuous recycle.
- $S^e = S$



NOTE : WHEN INTENTIONAL WASTING IS ACCOMPLISHED FROM THE AERATION BASIN $X^w = X$ AND $Q^e = Q^o - Q^w$

Figure 2. Complete Mixed Reactor with Cellular Recycle

(1) Substrate: The effluent substrate concentration, S^e, (that soluble fraction of the influent waste escaping treatment) for a system operating under constant environmental conditions and influent characteristics may be found by combining Equations (6) and (8) (Reference 5).

$$S = \frac{K_s(1+b\,\theta_c)}{\theta_c\,(Yk-b)-1} \qquad (11)$$

Thus, for a given microbial population with specified substrate utilization and growth coefficients, treatment efficiency at steady state is a function of the mean cell residence time.

(2) Biomass: A relationship for the steady state microorganism concentration in the aeration basin may be derived from a mass balance on the substrate through the system. Under steady state conditions the substrate concentration in the aeration basin is constant, therefore:

Mass rate of substrate in + Mass Rate of substrate utilization = Mass Rate of substrate out

$$Q^oS^o + V\frac{dS}{dt} = (Q^o-Q^w)S^e + Q^wS \qquad (12)$$

Recalling that $S^e = S$ and using Equations (3) and (5), it can be shown that:

$$X_a = \frac{\theta c}{\theta}\,\frac{Y(S^o-S)}{1+b\,\theta_c} \qquad (13)$$

(3) Mean Cell Residence Time: Similarly, a mass balance for the microbial mass in the treatment system may be formulated. Under steady state conditions the organism concentration in the aeration basin is constant:

Mass rate of organisms in + Mass Rate oMass organism growth = Mass Rate of organisms out

$$Q^oX_a^o + \frac{VdX_a}{dt} = (Q^oQ^w)X_a^e + Q^wX_a^w \qquad (14)$$

Assuming that wasting is accomplished directly from the aeration basin, substitutions involving Equations (1), (2), (6), and (8) yield the following expression for θ_c:

$$\theta_c = \frac{VX_a}{(Q^o-Q^w)X_a^e + Q^wX_a - Q^oX_a^o} \qquad (15)$$

Under steady state conditions the growth rate, $\Delta X/\Delta t$, is constant and represents the mass of organisms which must be wasted $(Q^o-Q^w)X_a^e + Q^wX_a$ to maintain a constant cell residence time. Because the net specific growth rate, μ, is derived from the substrate utilization and bacterial growth relationships, the implication is that θ_c, as defined by Equation

(15), applies only to those active organisms grown in the reactor. This, then, accounts for the $Q^o X_a^o$ term which must be subtracted as derived in the mass balance. In continuous flow activated sludge treatment systems a process control parameter which accurately describes the total system microbial mass is of interest. For this reason the operational definition for Θ_c has most often been defined (Reference 5) as:

$$\Theta_c = \frac{X_a V}{Q^e X_a^e + Q^w X_a^w} \tag{16}$$

Again, when wasting is accomplished from the aeration basin $Q^e = Q^o - Q^w$ and $X_a^w = X_a$.

(4) Θ_c^m : There exists a minimum cell residence time below which active cells will be washed out of the system at a rate which exceeds their growth rate. When this occurs $S^o = S = S^e$, thus, from Equation (6):

$$(\Theta_c^m)^{-1} = \frac{YkS^o}{K_s + S^o} - b \tag{17}$$

(5) Sludge for Disposal: From Equation (16) it is clear that the worst case with respect to excess sludge for disposal occurs when clarification efficiency is a maximum, i.e., $X^e = o$. If P_x equals sludge for disposal in mass/time units, then:

$$P_x = Q^w X^w = \frac{VX}{\Theta_c} \tag{18}$$

(6) Suspended Solids Balance: As described by Christensen (Reference 14), there are two different kinds of suspended solids commonly recognized: (1) the inorganic portion X_{in}, and (2) the organic portion X_v, generally termed volatile suspended solids:

$$X = X_{in} + X_v \tag{19}$$

where X represents total suspended solids. Further, X_v is considered to consist of four different organic fractions: (1) biodegradable suspended solids, X_d; (2) refractory suspended solids, X_r; (3) active organisms, X_a; and (4) inert organism remains after cellular decay, X_i.

Because X or X_v is most often used as a measure of X_a the relationship between Θ_c and the component fractions in X or X_v is of interest. If one assumes that the fraction of a particular suspended solids component in the effluent and waste stream is the same as its proportion in the reactor:

$$\Theta_c = \frac{X_a V}{Q^e X_a^e + Q_a^w X_a^w} = \frac{X_j V}{Q^e X_j^e + Q_j^w X_j^w} \tag{20}$$

where j can equal in, a, i, d, or r. For the case when X_a^o and $X_i^o = 0$ and further assuming that X_d^o degradation is proportional to S^o

degradation, a mass balance on each of the suspended solids components will lead to an expression for X_v or X as a function of Θ_c and Θ, given constant environmental and influent waste conditions. The term f_d represents the fraction of an active organism which is biodegradable.

$$X_v = \frac{\Theta c}{\Theta} \quad X_r^o + \frac{S}{S^o} \quad X_d^o + \frac{Y(S^o-S)}{1+b\,\Theta_c} \quad (1+(1-f_d)b\,\Theta_c) \tag{21}$$

and;

$$X = \frac{\Theta c}{\Theta} \quad X_{in}^o + X_v \tag{22}$$

Equation (21) is the fundamental design equation for complete mix suspended growth systems with or without cellular recycle while Equation (22) describes the operational solids retention time (SRT) used as the process control parameter.

$$SRT = \Theta_c = \frac{XV}{Q^e X^e + Q^w X^w} \tag{23}$$

2. HYDRAZINES AS PROCESS INHIBITORS

To date, very little research has been conducted on the effects of hydrazines in biological waste treatment systems. Tomlinson, Boon, and Tratman (Reference 15) conducted batch-screening tests on nitrifying activated sludge at various concentrations of neat hydrazine. They found that a concentration of 64 milligrams per liter (mg/ℓ) caused a 75-percent inhibition of ammonia oxidation and 48 mg/ℓ resulted in 75-percent inhibition of nitrite oxidation. That hydrazine was more toxic to Nitrobacter sp. than Nitrosomonas sp. in activated sludge was in general agreement with Meyerhof (Reference 16) who studied pure cultures of Nitrosomonas sp. and found 20-percent inhibition of ammonia oxidation at 32 mg/ℓ.

Yoshida and Alexander (Reference 17) used neat hydrazine as a selective inhibitor in their studies with Nitrosomonas europaea to show that hydroxylamine is an intermediate in the conversion of ammonia to nitrite. They reported that pure cultures exposed to 32 mg/ℓ immediately ceased nitrite formation, but the rate of nitrite generation at 3.2 mg/ℓ was still appreciable. Ammonium oxidation seemed to proceed even in the presence of 320 mg/ℓ hydrazine, as evidenced by an accumulation of hydroxylamine. Verstraete and Alexander (Reference 21) in their work on heterotrophic nitrification found that the growth of Arthrobacter sp. was inhibited at 32 mg/ℓ hydrazine but observed negligible effects at 3.2 mg/ℓ. Tomlinson concluded that concentrations in this range may not actually cause problems in treatment plants because (1) the nitrifying bacteria may acclimate with time, and (2) hydrazine may be destroyed, in part, by any heterotrophic population present. His recommendations included investigations into the feasibility of pretreating such industrial wastes in a high rate trickling filter or activated sludge process before attempting nitrification. To date, this assumption has not been verified. Currently there is no literature available on the effects of MMH or UDMH on either pure cultures or activated sludges.

SECTION III
EXPERIMENTAL METHODS AND MATERIALS

1. SUBSTRATE BASE

Throughout this investigation, primary effluent from the Tyndall Air Force Base (AFB) sewage treatment plant (STP) (Figure 3), was used as the raw feed. The Tyndall AFB facility, which treats 3.0 to 6.0 million liters (0.8 to 1.6 million gallons) of combined domestic and industrial wastewater per day, employs two single-stage trickling filters for secondary waste stabilization. Each rock packed filter is subjected to hydraulic loadings which range from 7.4 to 14.7 thousand liters/square meter/day (7.9 to 15.8 million gallons/Acre/DAY) (including 1:1 recirculation), the variation being a function of seasonal precipitation. The average organic loading is 16 Kg Biochemical Oxygen Demand (BOD)/cubic meter (M^3)/Day (23.2 lb BOD_L/1000 ft^3/DAY) per filter.

Characterization of the raw feed solution was undertaken to aid in designing the experiment and in an effort to quantify supplemental requirements. Analytical procedures, as outlined in Section III, paragraph 6 of this report, produced the data summarized in Table 1. The values represent an average of numerous data points collected over several months during the early stages of the study when system familiarization and troubleshooting runs were being made. From these data it was decided to enrich the raw feed by elevating the Chemical Oxygen Demand (COD) to 320 mg/ℓ with Carnation Slender®. The ingredients, as computed from data supplied by the manufacturer, are itemized in Table 2. Stoichiometric relationships were than developed which were used to predict relevant nitrogen/oxygen requirements and indirectly estimate phosphorous and alkalinity demands. Based on these results, the enriched feed could be supplemented to insure the final feed solution fit the experimental design.

TABLE 1. RAW FEED CHARACTERISTICS

PARAMETER	VALUE	UNITS
COD	100	mg/ℓ
BOD_5	85	mg/ℓ
Suspended Solids	62	mg/ℓ
Volatile Suspended Solids	50	mg/ℓ
NH_4^+-N	12.7	mg/ℓ
Organic -N	5.0	mg/ℓ
NO_3-N	None Detected	
NO_2-N	None Detected	
PO_4-P	6.0	mg/ℓ
Alkalinity (Total)	97.0	mg/ℓ as $CaCO_3$
pH	7.0	-

NOTE: All samples unfiltered.

TABLE 2. CARNATION SLENDER®

CONSTITUENT	VALUE, mg/ℓ
Measured COD	222,000
Carbohydrate	118,363
Protein	37,200
Fat	16,909
Ca	676
P	676
Mg	296
Fe	8.5
Zn	8.5
Cu	1.7
I	0.12

NOTE: Also contains vitamins A, C, D, E, B_6, B_{12}, Folic Acid, Thiamine, Riboflavin, Niacin, Biotin, and Pantothenic Acid.

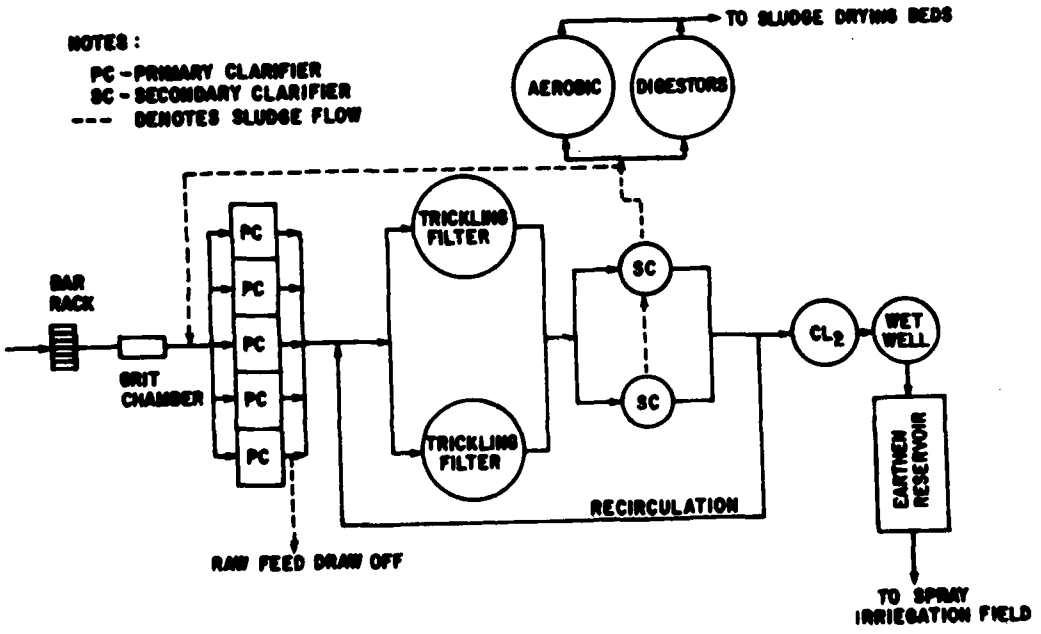


Figure 3. Tyndall Sewage Treatment Plant

2. SUPPLEMENTAL REQUIREMENTS

McCarty (Reference 6) has suggested that stoichiometric equations may be written for bacterially mediated reactions. This procedure establishes molar coefficients which may be used to predict electron acceptor utilization, cellular yield, and supplemental requirements. Such an analysis was performed on the enriched feed solution used in this study. The procedure is outlined in Appendix A. The supplemental nitrogen, phosphorous, oxygen, and alkalinity requirements derived from these calculations are discussed below.

a. Nitrogen(N): Calculations indicated that 19.2 mg/ℓ N would be required for heterotrophic synthesis. Based on the empirical formulations derived in Appendix A, it can be shown that the total organic-N available is 16.0 mg/ℓ. In addition, the raw feed solution contains 12.7 mg/ℓ inorganic-N (NH_3-N). Obviously there will be approximately 9.5 mg/ℓ-N remaining which should be available for nitrification. In an effort to insure nitrogen was not limiting and to increase the amount available for nitrification, 4.7 mg/ℓ urea-N was added to the enriched feed.

b. Phosphorous(P): To insure phosphorous was not limiting, the enriched primary effluent was supplemented with 5.2 mg/ℓ PO_4-P. This raised the total available phosphorous to 11.9 mg/ℓ compared to the demand of 3.0 mg/ℓ.

c. Oxygen(O_2): To insure an excess of dissolved oxygen (DO), humidified air was sparged through the mixed liquor at a rate of 4 liters/minute. Based on an air density of 1.2 grams (gm) /liter under the experimental conditions (1 atmosphere, 20 degrees celsius (^{0}C) and noting that air is 21 percent oxygen by weight, it can be shown that approximately 145 gm O_2/day were made available to the system. Assuming a conservative oxygen transfer efficiency of 5 percent (Reference 18), the calculated absorptive capacity is 7.2 gm O_2/day, or a 30-percent excess. Periodic checks on the mixed liquor to confirm a DO above 5 mg/ℓ would later insure that oxygen was not limiting during the investigation.

d. Alkalinity: While the estimates for alkalinity suggested a requirement of 2410 mg/ℓ (as $CaCO_3$), actual demands established during the initial stabilization period were much less. It was found that the pH could be maintained above 7.0 by supplementing the enriched feed with only 260 mg/ℓ $NaHCO_3$ (157 mg/ℓ as $CaCO_3$). This is due, in part, to the significant stripping of CO_2 from solution under actual operating conditions.

TABLE 3. FEED SOLUTION MAKE-UP

Constituent	Formulation	Mass Addition	Supplemental Value (mg) Measured	Theoretical***
Enriched Feed	$C_{54}H_{96}O_{20}N_7$*	223 mg** (1ℓ)		
COD			320	386
ORG-N			-	16.0
PO_4-P			6.7*	—
NH_4^+-N			12.7	-
ALKALINITY			97	-
Supplements				
UREA	NH_2CONH	0.010 gm	-	4.7 as N
POTASSIUM PHOSPHATE	K_2HPO_4	0.026 gm	-	5.2 as P
SODIUM BICARBONATE	$NaHCO_3$	0.26 gm	-	157 as $CaCO_3$

* Empirical (Appendix A)

** Measured 1° eff. value (VSS) + Slender® component as documented by Carnation

*** Based on empirical formulation and mass addition.

TABLE 4. FINAL FEED SOLUTION
(All values in mg/ℓ)

Constituent	Theoretical *	Measured
COD	386	320
Org-N	20.7	20.3
NH_4^+-N	-	12.7
Total-N	33.4	29.8
PO_4-P	11.9	10.0
Alkalinity	254 as $CaCO_3$	275 as $CaCO_3$
VSS	-	100
SS	-	112

*Appendix A.

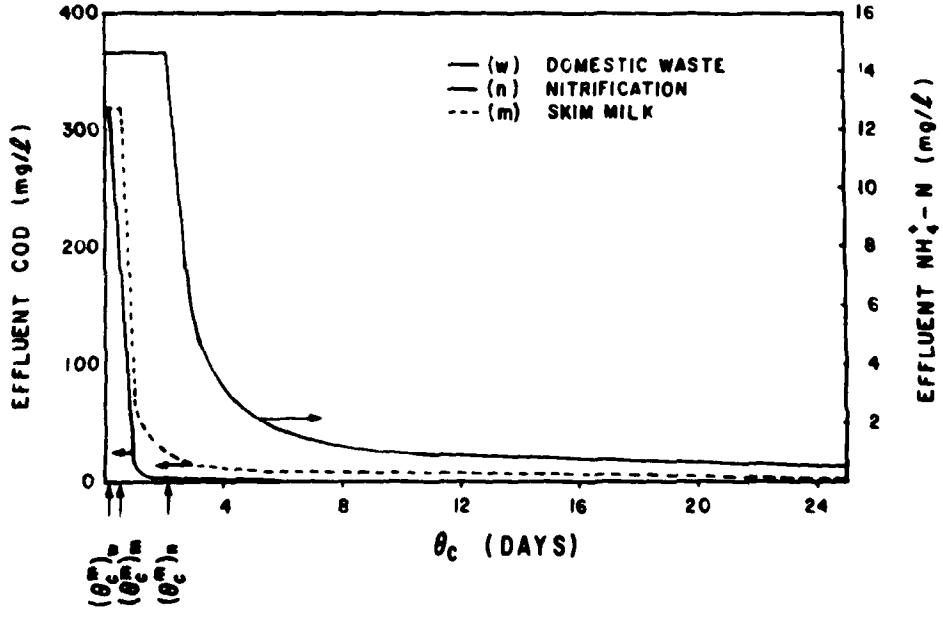


Figure 4. Theoretical Effluent COD and Ammonia Nitrogen as a Function of Mean Cell Residence Time

3. OPERATING PARAMETERS

Knowing the bacterial growth and substrate utilization coefficients for a particular waste under specified environmental conditions, Equation (11) may be used to relate effluent soluble substrate concentration to mean cell residence time. Using the coefficient data summarized in Table 5 for COD removal (domestic waste, skim milk) and nitrification, the relationship in Figure 4 results.

It is clear from Figure 4, that in order to insure viable heterotrophic and autotrophic populations during this laboratory investigation, a cell residence time of at least six days should be maintained. In a laboratory environment, it is generally more desirable to monitor and maintain a constant Θ and X_v or X in an effort to realize Θ_c*. For the mixed treatment system of interest here, X_v can be described by a modification of Equation (27):

$$X_v = \frac{\Theta_c}{\Theta} \left[X_r^o + \frac{S}{S^o} X_d^o + \frac{Y(S^o-S)}{1+b\,\Theta_c}(1+(1-f_d)b\,\Theta_{c_H}) + \frac{Y(S^o-S)}{1+b\Theta_c}(1+(1-f_d)b\,\Theta_{c_A}) \right] \quad (24)$$

and recall that:

$$X = \frac{\Theta_c}{\Theta} X_{in}^o + X_v$$

where the subscripts H and A stand for heterotrophic and autotrophic, respectively. The autotrophic biomass is, however, only about four percent that of the heterotrophic, the inference being that the last term in Equation (24) can be dropped. Designing for a Mixed Liquor Suspended Solids (MLSS) of 4500 mg/ℓ** a constant hydraulic detention time of 6.67 hours, and using the skim milk coefficients (conservative), Equations (11) and (23) lead to a Θ_c of 7.5 days. These parameters are summarized in Table 6.

*Under constant influent and environmental conditions the growth rate will remain constant ($S^o >> K_s$). When this situation is accompanied by efficient clarification, the amount of mixed liquor wasted to maintain the design MLSS will be constant and Θ_c will, therefore, also remain constant.

** Assumptions: $X_a^o = X_i^o = 0$

$$X_r^o = 0.35\, X_v^o$$

$$X_d^o = 0.65\, X_v^o$$

TABLE 5. BACTERIAL GROWTH AND SUBSTRATE UTILIZATION COEFFICIENTS

TREATMENT OBJECTIVE	COEFFICIENT	DOMESTIC SEWAGE VALUE	DOMESTIC SEWAGE REFERENCE	SKIM MILK VALUE	SKIM MILK REFERENCE	BASIS
COD Removal	Y	0.45	5	0.48	4	mg Cells/mg COD
	b	0.05	5	0.05	4	Day^{-1}
	k	20.9*	2	6.0*	3	mg COD/mg Cells-Day
	K	60	2	110	3	mg/ℓ COD
Nitrification	Y	0.36	5	-	-	mg Cells/mg NH_4^+-N
	b	0.05	5	-	-	Day^{-1}
	k	1.8	5	-	-	mg NH_4^+-N/mg Cells-Day
	K_s	3.6	5	-	-	mg/ℓ NH_4^+-N

* The references for these values reported μ_m where $\mu_m = Yk$ k was calculated based on the Y value given in this table.

NOTE: Values calculated for cell yield, Y, based on the stoichiometry developed in Appendix A are:
Heterotrophic: 0.46 mg/cells/mg COD
Autotrophic: 0.36 mg/cells/mg NH_4^+-N

TABLE 6. DESIGN OPERATING PARAMETERS

Θ	MLSS*	Θ_c
6.67 Hours	4500 mg/	7.5 Days

*The first two neat hydrazine runs (20/10, 6/3) deviated slightly from the design MLSS value of 4500 mg/ℓ. The target MLSS concentrations were: 5600 mg/ℓ for reactors 1 to 4 (20/6 mg/ℓ) and 4000 mg/ℓ for reactors 9 to 12 (10/3 mg/ℓ). Two controls were operated at each MLSS concentration. These values correspond to Θ_c's of 10 and 6.5 days, respectively. Solids were maintained as outlined in Table 6 for all subsequent experimentation.

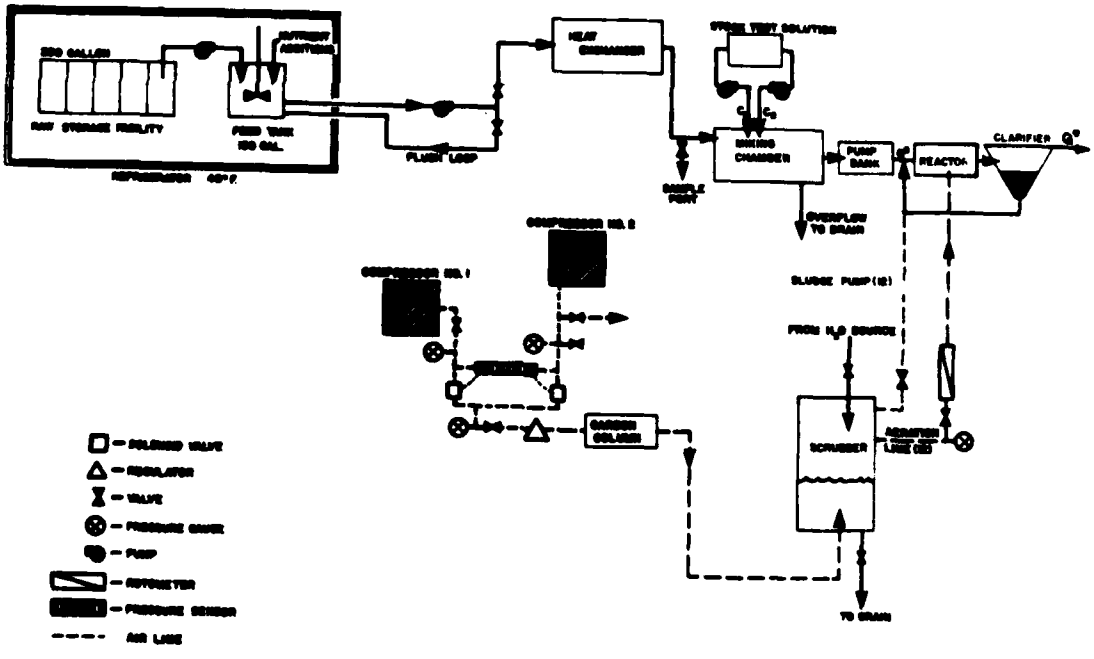


Figure 5. Laboratory Schematic

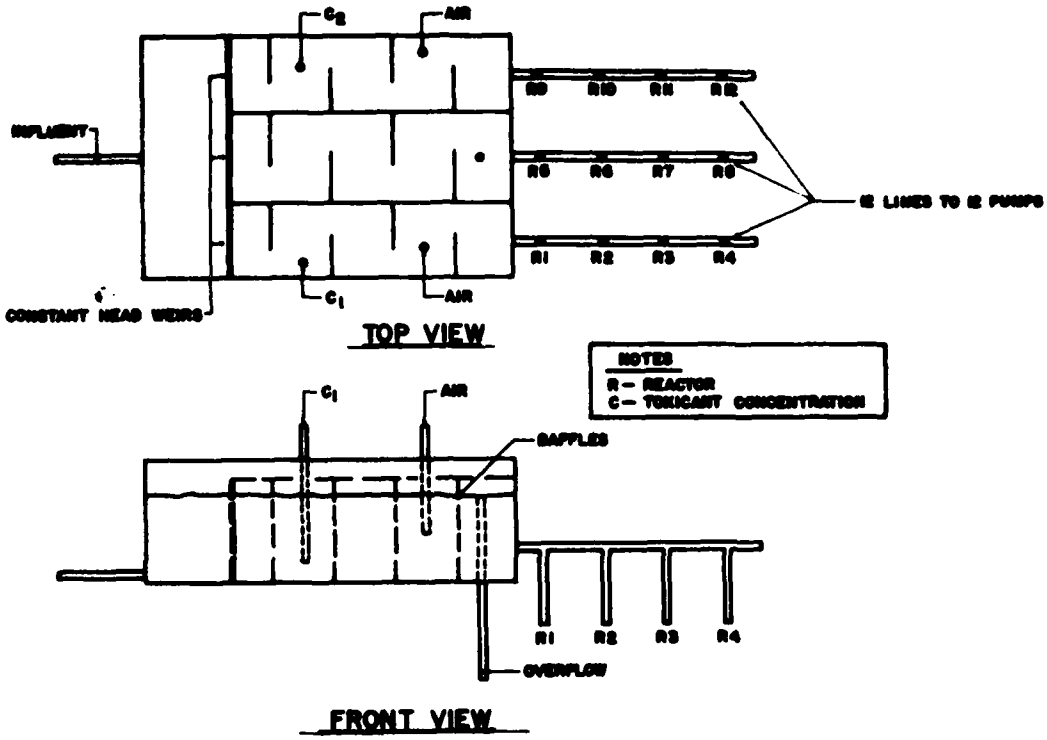


Figure 6. Mixing Chamber Used to Achieve C_1 in Reactors 1 to 4, C_2 in Reactors 9 to 12, and Control Conditions in Reactors 5 to 8 During Continuous Feed Studies

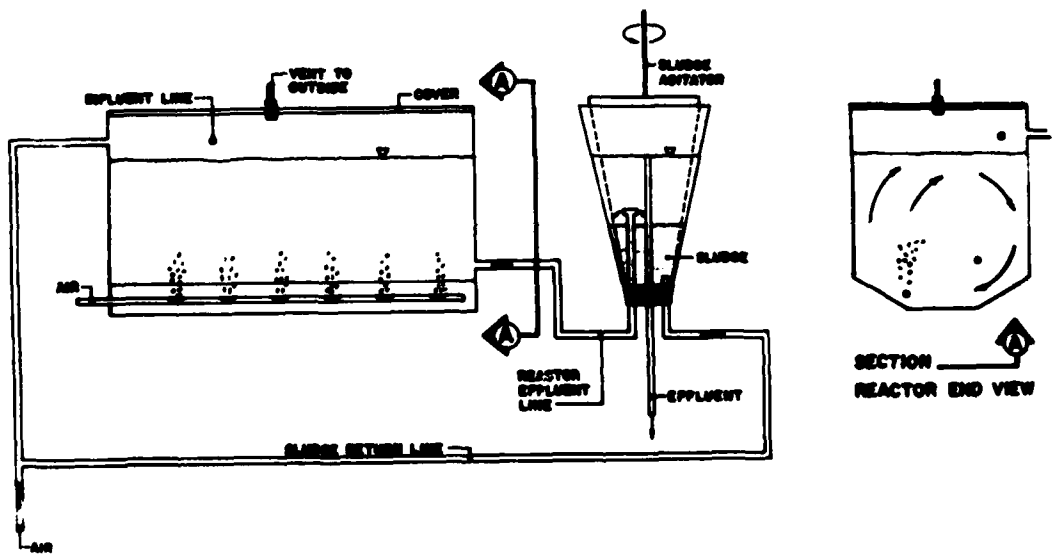


Figure 7. Aeration Basin and Clarifier

4. BENCH SCALE SYSTEM

Figure 5 is a schematic of the laboratory system developed for continuous flow studies. The reactors were initially seeded with mixed liquor from the Panama City conventional activated sludge plant and subsequently maintained as summarized below.

Several afternoons each week 200 gallons of primary effluent were withdrawn just upstream from the Tyndall AFB STP trickling filters and immediately transported to the Environics Laboratory located approximately one mile from the plant. At this point the wastewater was transferred to five 151-liter (40-gallon) containers inside a refrigeration unit (4.4°C) adjacent to the laboratory. All raw feed was stored in this configuration until utilized as substrate base, but in no case did the storage time exceed four days.

The raw feed, having been enriched and supplemented in the feed tank, was pumped through a heat exchange (25°F) and then into the mixing chamber, illustrated in Figure 6. This chamber was designed such that two continuous feed toxicant concentrations could be evaluated simultaneously. As indicated, the center channel received only the supplemented feed solution, serving the control series of reactors. The 6-liter Plexiglas® aeration basins detailed in Figure 7 were supplied with humidified air passed through an activated carbon filter to affect excess dissolved oxygen and complete mixing. Sludge return from the 2-liter Pyrex® clarifiers was maintained using gravity induced draw-off and an in-line air pump.

5. EXPERIMENTAL MATRIX

The continuous feed studies were conducted over a wide range of fuel concentrations, specifically 20, 10, 6, 3, 1.0, and 0.5 mg/ℓ. Four reactors were evaluated at each concentration in addition to four controls operated throughout the study. Because two concentrations could be evaluated simultaneously, a total of three runs were performed for each fuel. These have been designated 20/10, 6/3, and 1/.5 with the numbers referring to the target fuel concentrations.

Slug loading experiments were performed at concentrations of 250, 125, 50, and 25 mg/ℓ (based on 6) on duplicate continuous flow reactors. These concentrations were realized by adding from 1 to 12 milliliters (ml) of stock fuel solutions directly to the aeration basin.

In the slug studies effluent characteristics were monitored for sufficient time to make inferences about process recovery. All reactors were allowed to achieve steady state as indicated by effluent COD and NO_3^--N concentrations prior to initiating hydrazine feeds for any one particular evaluation. Table 7 summarizes the seeding/evaluation sequence employed.

TABLE 7. SEEDING/EVALUATION SEQUENCE

FUEL	ACTION
	Initial Seeding
HZ	20/20 Run
	6/3 Run
	1/0.5 Run
	Slug Loads
	Reseed
MMH	20/10 Run
	6/3 Run
	1/0.5 Run
	Reseed
	Slug Loads
UDMH	Slug Loads
	20/10 Run
	1/0.5 Run
	6/3 Run

6. ANALYTICAL PROCEDURES

a. General: Those parameters of interest included the major forms of nitrogen (NH_3, organic, NO_3^-), COD, total and volatile suspended solids, HZ, MMH, UDMH and pH. Orthophosphate and alkalinity were monitored less frequently. All assays were performed in accordance with Standard Methods for the Examination of Water and Wastewater, 14th edition. Specific techniques are outlined in Table 8. Notable exceptions and comments are summarized below.

b. Hydrazine: The colorimetric method described by Watt and Chrisp (Reference 19) was used for all HZ and MMH assays. This procedure is based on a stable yellow color which develops upon addition of p-dimethyl-aminobenzaldehyde to dilute solutions of hydrazine. Absorbance was measured at 460 anometers (nm) using a Coleman 55 digital spectrophotometer.

UDMH determinations were accomplished using the colorimetric method outlined by Pinkerton, Lauer, Diamond, and Tamas (Reference 20). The procedure develops a colored solution using trisodium pentacyanoamino ferroate (TPF) and a disodium acid phosphate/citric acid buffer. During this investigation the recommended buffer concentrations were increased by a factor of 3.5 to increase sensitivity. It was also found that a wavelength of 495 anometers (nm) provided greater accuracy than the recommended 500 anometers (nm).

c. Schedule: Five days each week mixed liquor samples were collected and immediately analyzed for total and volatile suspended solids. Filtered effluent samples (Whatman #40) were used in the determination of NO_3^--N, COD, and pH. Unfiltered aliquots of these same samples were

assayed for NH_4^+-N and organic -N. Unfiltered influent samples were analyzed for these same parameters. Both influent and effluent were intermittently checked for orthophosphate, alkalinity, and suspended solids. Qualitative microscopic examinations of the mixed liquor were also conducted on an irregular basis throughout the investigation. Wasting was accomplished once daily directly from the aeration basin to realize the desired MLSS. During continuous flow hydrazine studies, influent fuel concentrations were assayed at least once daily from each reactor.

TABLE 8. ANALYTICAL TECHNIQUES

Parameter	Method	Reference Standard Methods
COD	Dichromate Digestion	508
Suspended Solids	Membrane Filter, Residue on Evaporation	208D
Volatile Suspended Solids	Membrane Filter, Residue Residue on Ignition	208G
NH_3-N	Distillation/Titrimetric*	418A/D
NO_3-N	Electrode**	419B
Organic-N	Digestion/Distillation/ Titrimetric	412/418D
Alkalinity	Titrimetric to pH 4.3	403
pH	Electrode	424
PO_4-P	Colorimetric	425D

* Oxidized nitrogen interference not detected.

** Comparisons with Brucine method yielded good correlation.

SECTION IV

RESULTS - HYDRAZINE (HZ)

Neat hydrazine is a colorless liquid with a density of 1.000 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125 mg/l stock solution resulted in 0.23 mg COD/mg HZ and no detectable ammonia or organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. HZ Degradation: Although it was the objective of this study to maintain stable hydrazine concentrations during each run, actual analyses showed that there was some variation. Figure 8 shows the measured HZ concentrations in the influent to the reactors. Each point represents the average of four reactors, and as can be seen, the percent variation was greater in the lower concentration studies. Experiments attempted at 1 mg/l actually represent exposure between 0.6 mg/l and 0.9 mg/l. Those designed for 0.5 mg/l were measured to be between 0.2 mg/l and 0.4 mg/l. The theoretical and measured average influent and effluent hydrazine concentrations for the continuous feed studies are summarized in Table 9. It is apparent that degradation of HZ occurs at all influent concentrations investigated. Because degradation by atmospheric oxidation was not observed in control studies where tap water was substituted for the activated sludge (see Figure 17, paragraph 2a, this section), the documented reductions in HZ are assumed to be the result of microbial metabolism.

b. COD: Table 10 summarizes the influent and control reactor effluent data for the continuous feed studies. While the mean influent values were very close to the target of 320 mg/ℓ for all runs, the standard deviations suggest a wider than optimal range for individual values. Figure 9 shows the daily influent data as well as the mean effluent CODs from the four control reactors. As can be seen, effluent quality remained very stable in the controls despite influent COD fluctuations. These findings agree with data presented by Saheh and Gaudy (Reference 22) who have reported that recycle systems can handle a 200-percent step change in influent organic substrate concentration with only a small, short-lived disturbance in effluent quality. They have further stated that when a constant recycle rate is employed, as was the case in the present study, such step increases can be accommodated with little or no change in effluent quality. Note also that the data presented are for unfiltered samples. The standard deviations on the filtered influent CODs were consistently smaller.

Remaining COD in the clarifier effluent as a function of influent HZ concentration and time is shown in Figure 10. For the operating parameters in this study, a HZ concentration of approximately 3 mg/ℓ causes no reduction in treatment efficiency. Concentrations above 10 mg/ℓ result in the complete loss of COD removal capabilities within a few days.

Effluent organic nitrogen is related to effluent COD, as shown in Figure 11. Microscopic examinations of exposed activated sludge samples

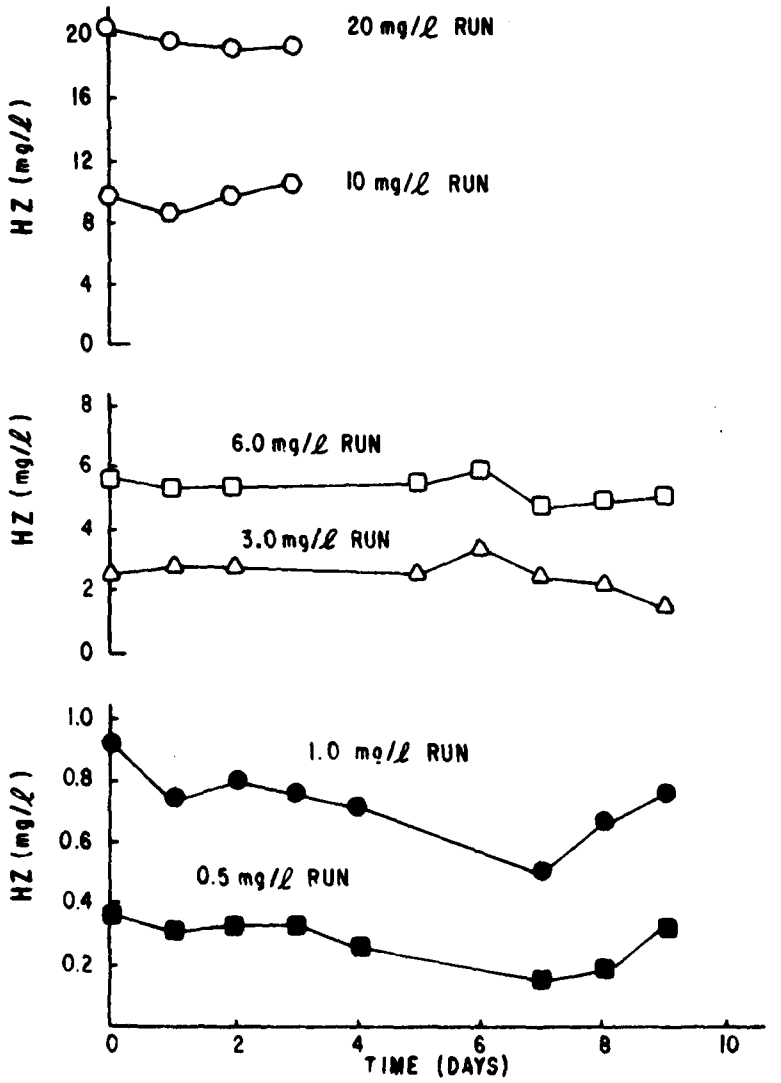


Figure 8. Continuous Influent HZ Concentrations

TABLE 9. HZ CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/ℓ)

Theoretical	Study Designation	Influent Mean	Influent σ	Influent n	Effluent Mean	Effluent σ	Effluent n	Reduction Percent
20	20/10	19.7	0.9	22	6.1	2.0	26	69
10	20/10	9.6	0.8	22	2.1	0.9	26	78
6.0	6/3	5.4	0.7	44	0.4	0.3	56	93
3.0	6/3	2.7	0.6	43	0.1	0.1	52	96
1.0	1/0.5	0.7	0.1	52	ND	0.0	46	∿100
0.5	1/0.5	0.3	0.1	52	ND	0.0	36	∿100

NOTE: ND = None Detected

TABLE 10. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/ℓ) Mean	Influent COD (mg/ℓ) σ	Control Effluent COD (mg/ℓ) Mean	Control Effluent COD (mg/ℓ) σ	Control Percent Removal
20/10	3	324	135	56	9	83
6/3	8	307	35	59	7	81
1/0.5	9	311	56	44	4	86
Overall	-	314*	67	52**	10	83

* n = 20
** n = 78

TABLE 11. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/ℓ)

Study	Study Length (Days)	Influent NH_3-N Mean	Influent NH_3-N σ	Influent TKN Mean	Influent TKN σ	Control Effluent NH_3-N Mean	Control Effluent NH_3-N σ	Control Effluent NO_3-N Mean	Control Effluent NO_3-N σ	Nitrification* Percent In Controls
20/10	3	12.5	2.6	29.9	7.2	0.0	0.1	20	2.5	78
6/3	9	14.1	4.3	28.0	4.8	0.1	0.2	22	4.5	79
1/0.5	9	14.4	3.8	27.6	5.7	0.0	0.1	23	2.7	83
Overall	-	13.8	3.7	27.4	4.9	0.1	0.1	22	3.6	80

*Based on TKN Conversion to NO_3-N

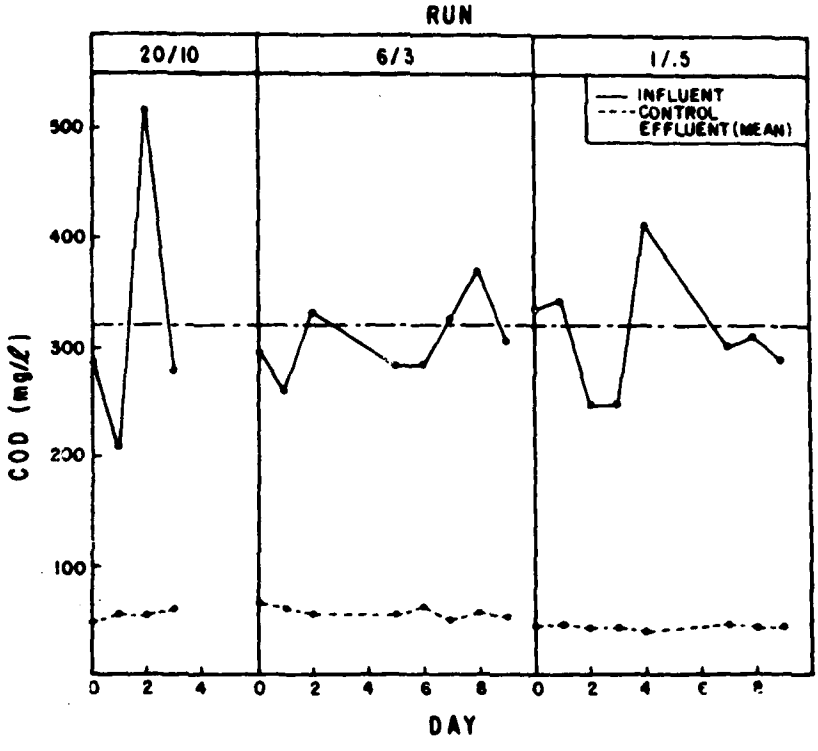


Figure 9. *Influent COD and Mean Control Effluent COD* Values During Continuous Feed HZ Runs

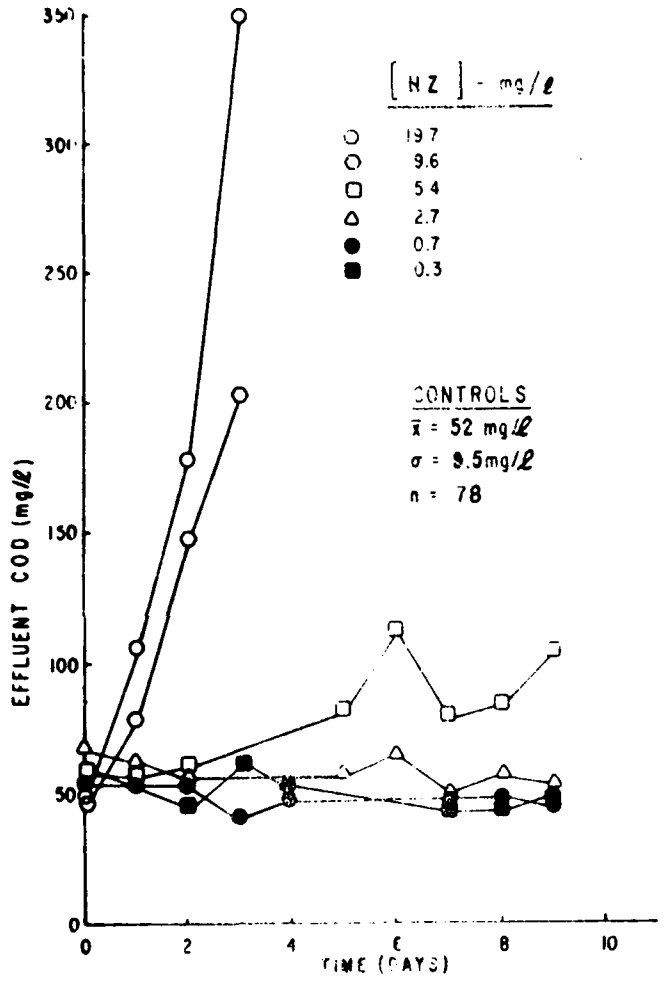


Figure 10. Effluent COD as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

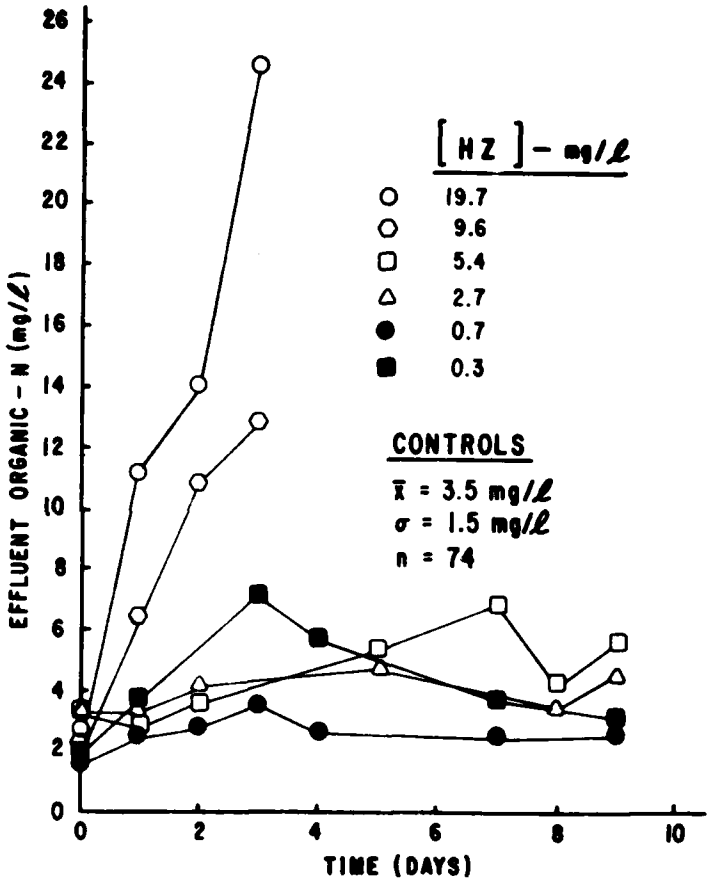


Figure 11. Effluent Organic Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

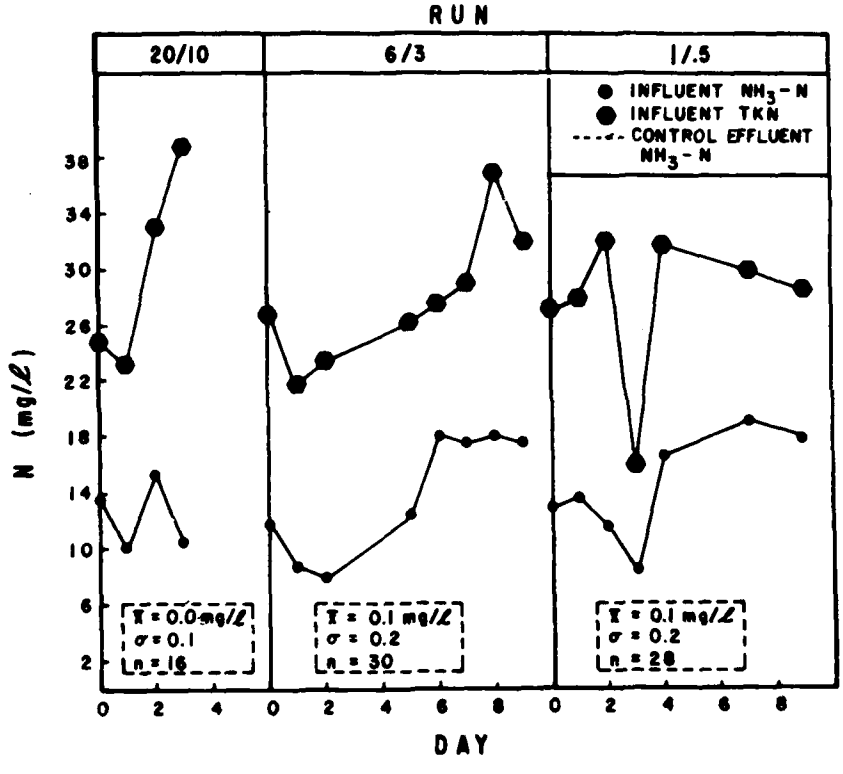


Figure 12. Influent and Control Effluent Nitrogen Data During Continuous Feed HZ Runs

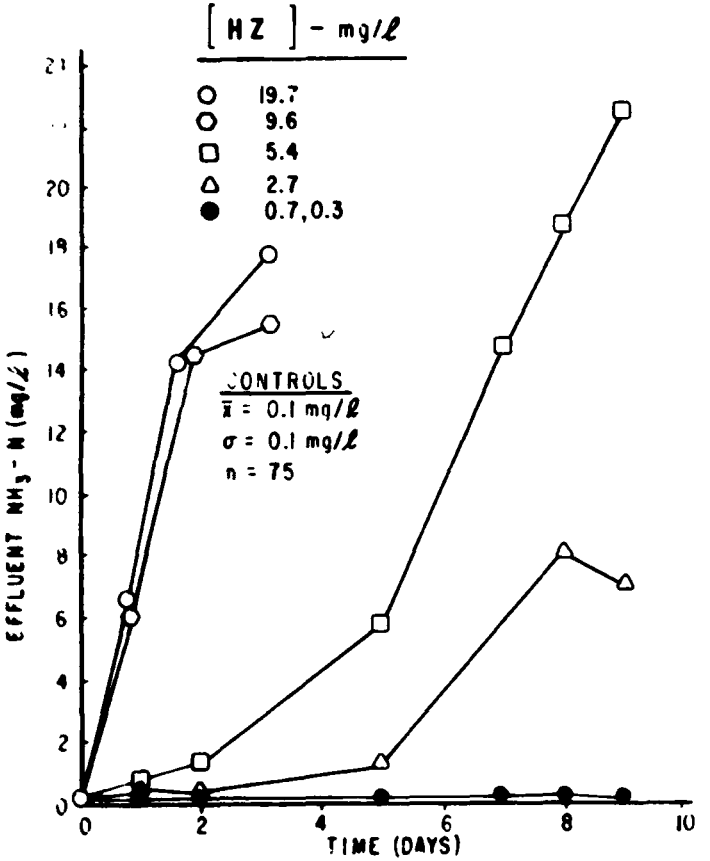


Figure 13. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed HZ Concentration (Mean of 4 Replicates)

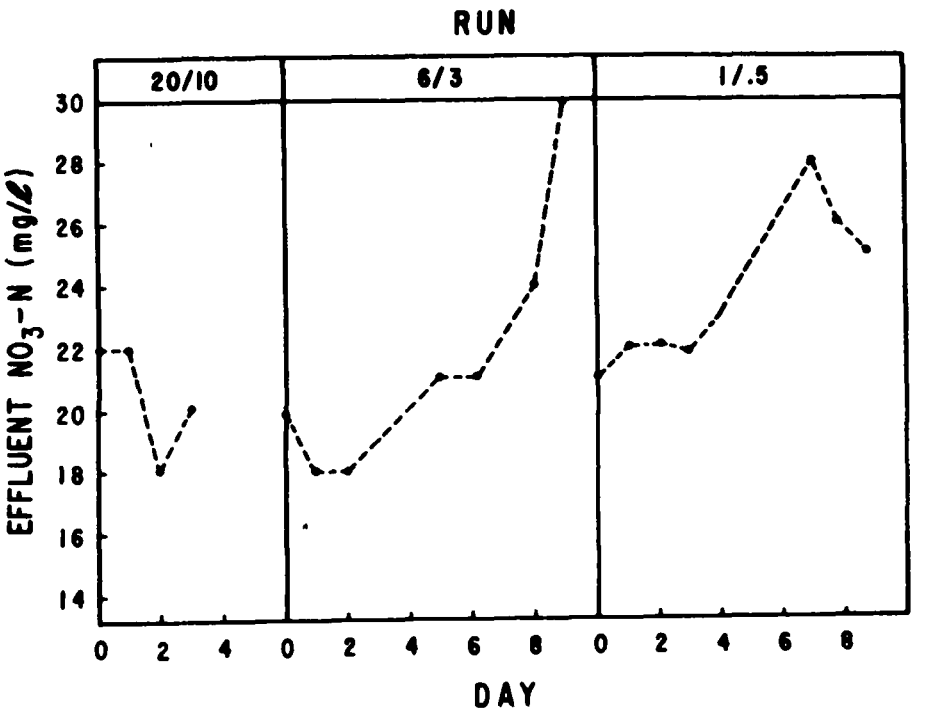


Figure 14. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed HZ Runs

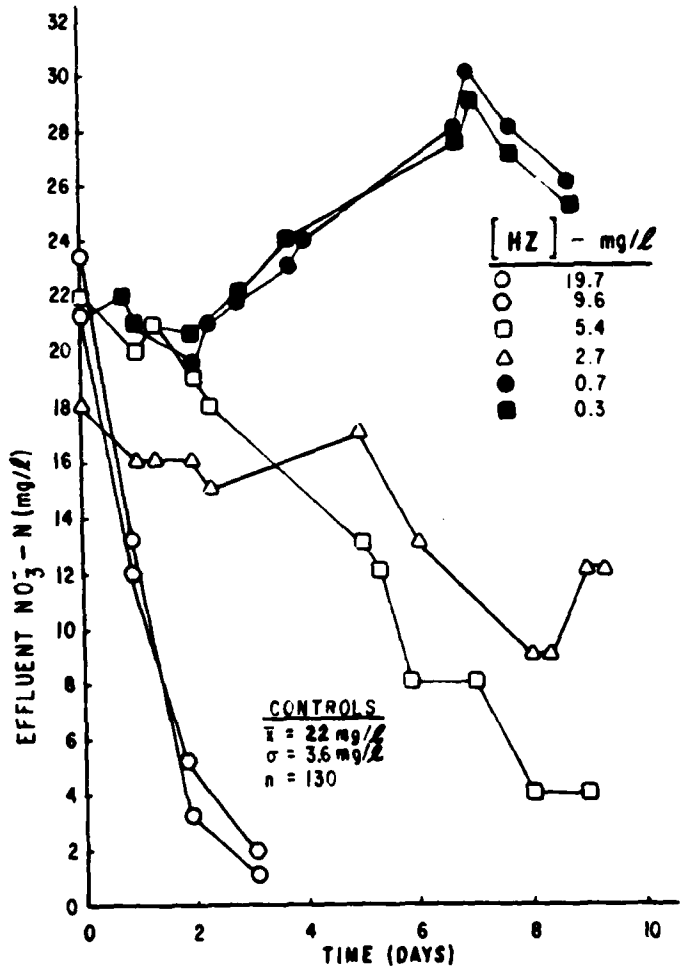


Figure 15. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed HZ Runs (Mean of 4 Replicates)

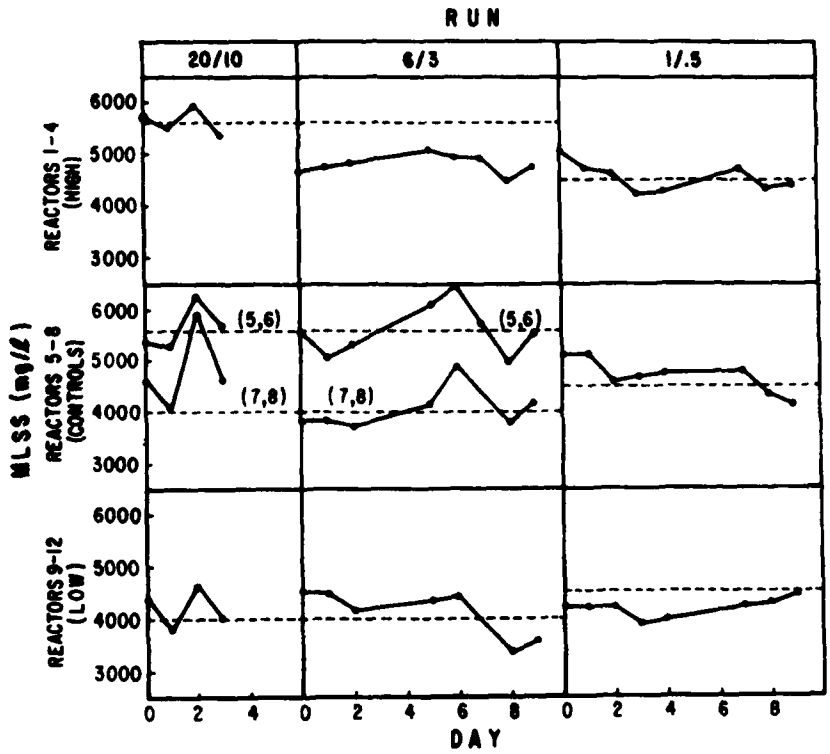


Figure 16. Mean MLSS During Continuous Feed HZ Runs (Mean of 4 Replicates Except Controls During 20/10 and 6/3 Which Were Duplicates)

verified that significant cell lysis was affected by HZ, releasing soluble organic nitrogen and other organics which contributed to soluble effluent COD as well.

c. Nitrification: The influent and control effluent nitrogen data collected over the continuous feed HZ studies are summarized in Table 11. Overall, 80-percent nitrification of influent TKN was achieved during these experiments. Effluent ammonia concentrations agreed well with those predicted based on the growth and substrate utilization coefficients discussed in Section III of this report. (Figure 4).

As for COD, the daily influent and control effluent parameters of interest have been graphically displayed in Figures 12 and 14 for comparison with daily effluent qualities in those reactors receiving HZ. The data in Figure 12 clearly indicates that while influent ammonia and TKN varied somewhat from day to day, effluent ammonia concentrations were consistently below 0.2 mg/ℓ. From Figure 13 it is apparent that even low HZ concentrations ($\sim$3 mg/ℓ) cause inhibition of nitrification. The nitrate data presented in Figure 15 agree well with the ammonia data. As effluent ammonia increases, effluent nitrate decreases. The combined NH_3 and NO_3 data suggest that HZ is definitely toxic to Nitrosomonas sp. in this range. Because the conversion of ammonia to nitrite is generally considered to be the rate limiting step in the oxidation scheme, no such inferences can be made with respect to Nitrobacter sp.

d. Suspended Solids: The suspended solids data for the control reactors are outlined in Table 12. Recall that, during the 20/10 and 6/3 runs, the high reactors (20 and 6 mg/ℓ) were operated at an MLSS of 5600 mg/ℓ while the low reactors (10 and 3 mg/ℓ) were held at 4000 mg/ℓ.

TABLE 12. CONTROL MLSS DATA (mg/ℓ)

	HIGH			LOW		
Study	Mean	σ	n	Mean	σ	n
20/10	5660	450	8	4830	860	8
6/3	5600	570	16	4060	500	14

	MEAN	σ	n
1/0.5	4470	530	32

The MLSS response to HZ are summarized in Figure 16. As in Table 12, all values represent concentrations prior to wasting to the desired levels. Wasting was accomplished once daily if the MLSS concentration was above the target value. Both HZ and influent COD affected MLSS. Step increases in influent COD generally resulted in increased MLSS values as, for example, on day 2 of the 20/10 run. While HZ concentrations from 10 to 20 mg/ℓ caused increased effluent organic nitrogen concentrations (Figure 11) and therefore effluent suspended solids, the majority of which were lysed cells (qualitative observation), the loss of solids was not of sufficient magnitude to decrease MLSS and hence Θ_c significantly during any of the runs.

2. SLUG FEED STUDIES

a. HZ Degradation: Figure 17 is a plot of the ratio reactor HZ concentration (C) over the initial added HZ concentration (C_o) versus time. The initial drop in the control plot is due to the dilution effected by the clarifier volume. As in the continuous feed studies, there is significant degradation of the hydrazine even at an initial hydrazine concentration of 243 mg/ℓ. Assuming exponential bacterial decay of the hydrazine, it is possible to calculate a bacterial decay constant (K) from Equation (25).

$$\ln C/C_o = -\frac{1}{\Theta_s} + Kt \qquad (25)$$

C = HZ at time t (mg/ℓ)

C_o = HZ at time 0

Θ_s = Total system (reactor plus clarifer) hydraulic detention time (HR) = 7.78 HR

t = Time (HR)

K = Bacterial Decay Constant (HR^{-1})

If hydrazine was not toxic to the activated sludge fauna, Equation (25) would predict that K would be independent of C_o. This was not observed, as shown in Table 13 and in Figure 18, which is a plot of the calculated half-life ($t_{1/2}$) of hydrazine at each added concentration.

TABLE 13. BACTERIAL DECAY CONSTANTS FOR HZ

Initial HZ (mg/ℓ)	K (HR^{-1})	Correlation Coefficient (R)
23	0.498	0.9730
44	0.353	0.9912
119	0.246	0.9914
243	0.160	0.9916

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 14.

TABLE 14. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/ℓ)

HZ		Influent			MLSS	
Theoretical	Measured	COD	NH_3-N	ORG-N	Mean	σ
250	243	338	18.7	15.4	5030*	850
125	119	337	17.2	14.8	4260	46
50	44	319	13.0	15.3	4700*	113
25	23	340	14.6	6.5	4130	615

*Wasted to 4500 mg/ℓ

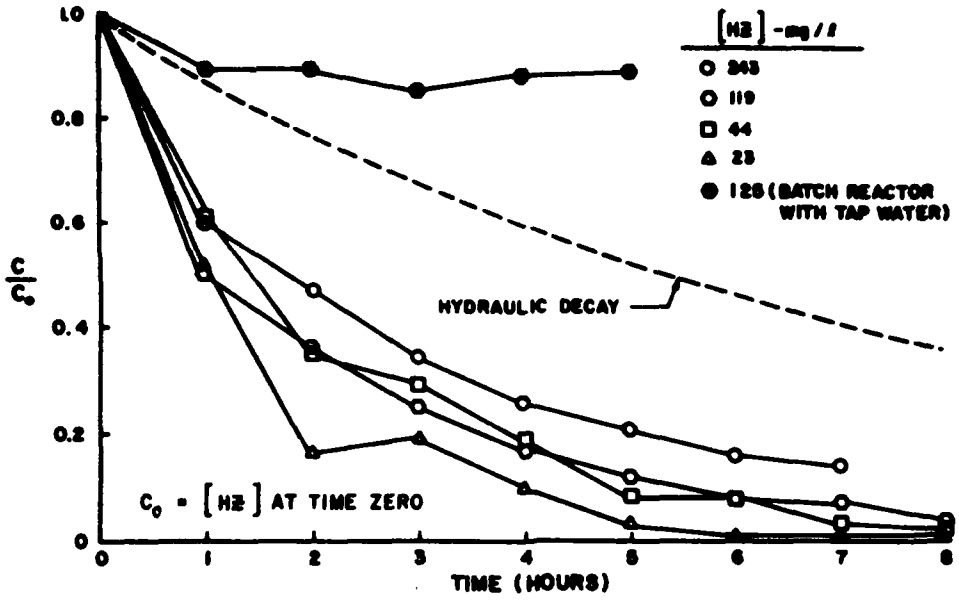


Figure 17. HZ Degration During HZ Slug Feed Experiments (Mean of Duplicates)

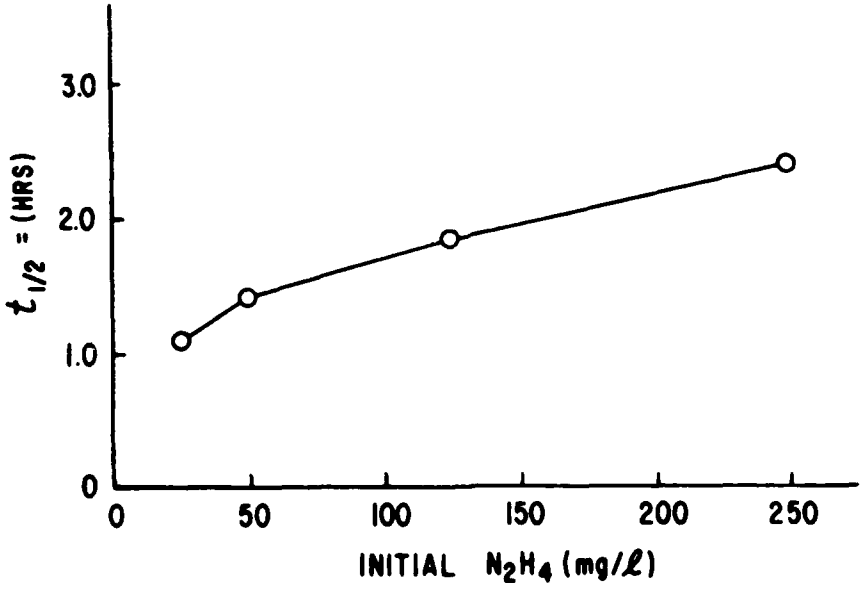


Figure 18. Calculated Half Life for HZ as a Function of Initial HZ Slug Concentration

(1) COD: Figure 19 shows that, as would be expected from the continuous feed studies, the high initial hydrazine concentrations caused an immediate decrease in treatment efficiency. Of the 146 mg/ℓ COD in the effluent at one hour, only 33 mg/ℓ can be attributed to HZ. The 243 mg/ℓ samples were inadvertently lost because they exceeded the maximum value (400 mg/ℓ) for the COD protocol employed. Although there was some apparent effect at all the concentrations tested, the reduction of treatment efficiency, as measured by COD removal, would be minor for slug doses which did not increase the concentration to above 44 mg/ℓ N_2H_4. Figure 20 clearly shows that effluent organic nitrogen concentrations were elevated from 0 to 6 times initial values depending on the HZ slug.

(2) Nitrification: The effect of HZ slug feeds on nitrification is shown in Figures 21 and 22. Even at 23 mg/ℓ there is immediate inhibition. The nitrate decay rate is approximately equal to that expected for a completely mixed reactor with no influent nitrate, confirming that at all concentrations the oxidation of ammonia to nitrate has ceased.

c. Recovery: One of the objectives of this investigation was to document the time required to recover process efficiency following slug hydrazine exposures. The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 23.

(1) COD: Figure 24 illustrates that even for the 243 mg/ℓ study there was significant recovery within 4 days and complete recovery within 6 days. Recovery from HZ concentrations below 44 mg/ℓ was complete after approximately 3 days.

(2) Nitrification: Recovery of the nitrifying bacteria is slower than for the heterotrophs. In Figure 25 it can be seen that ammonia oxidation had not returned to normal until after 7 to 10 days. There appears to be an additional lag of from 1 to 8 days until a viable Nitrobacter sp. population is reestablished as indicated by Figure 26, suggesting that HZ is toxic to this species as well.

(3) Suspended Solids: As noted earlier, the slug doses of 243 mg/ℓ and 119 mg/ℓ produced significant cell lysis, the end result being increased solids in the effluent. Figure 27 indicates that at 243 mg/ℓ the MLSS dropped to a low of approximately 2000 mg/ℓ for about 4 days while those reactors receiving 119 mg/ℓ HZ declined to approximately 3000 mg/ℓ in this same time frame. Recovery at these high concentrations was not complete until 12 to 14 days post exposure. The 44 mg/ℓ and 23 mg/ℓ slug reactors were not significantly affected with respect to MLSS concentrations although effluent solids increased slightly for the first few days following introduction of the HZ.

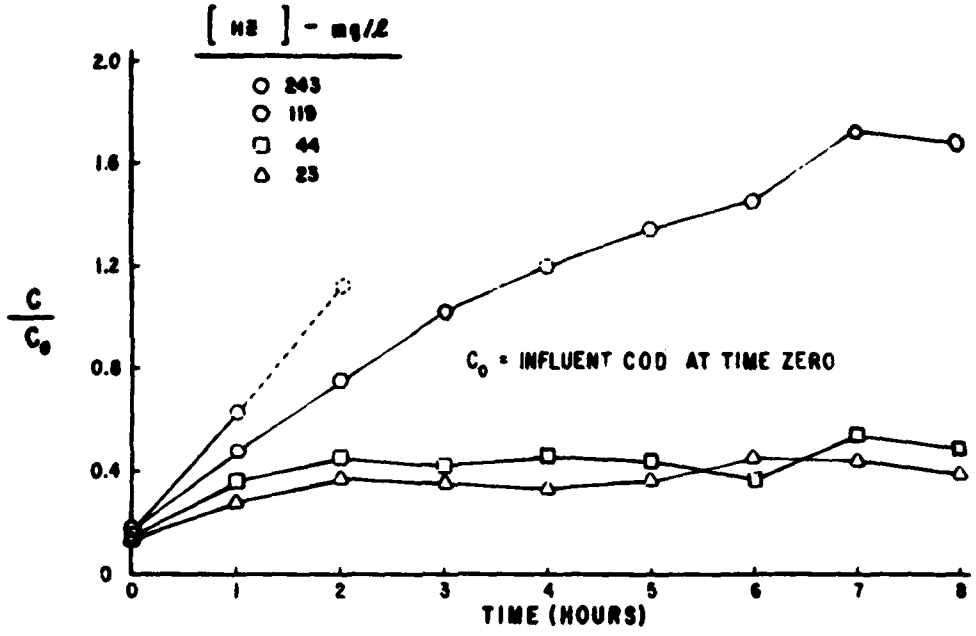


Figure 19. Acute Effluent COD Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

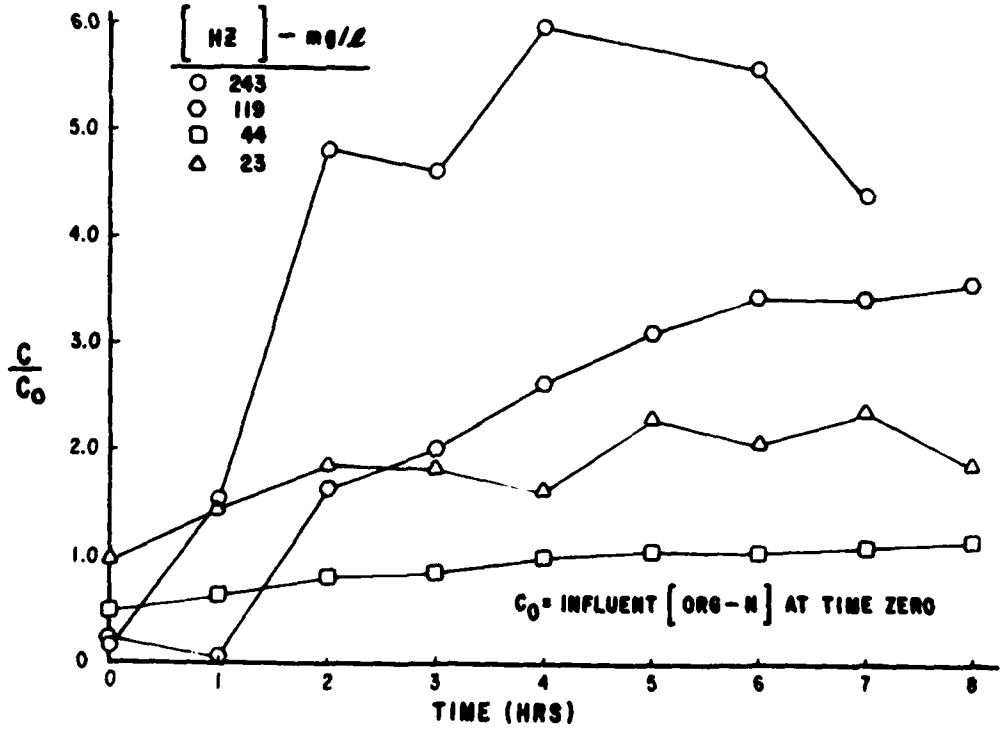


Figure 20. Acute Effluent Organic Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

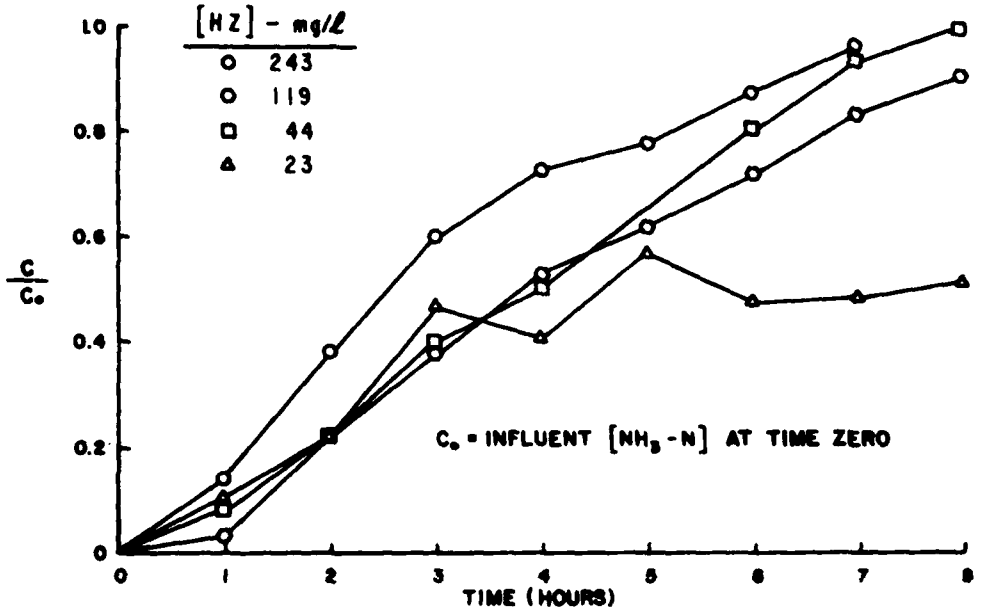


Figure 21. Acute Effluent Ammonia Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

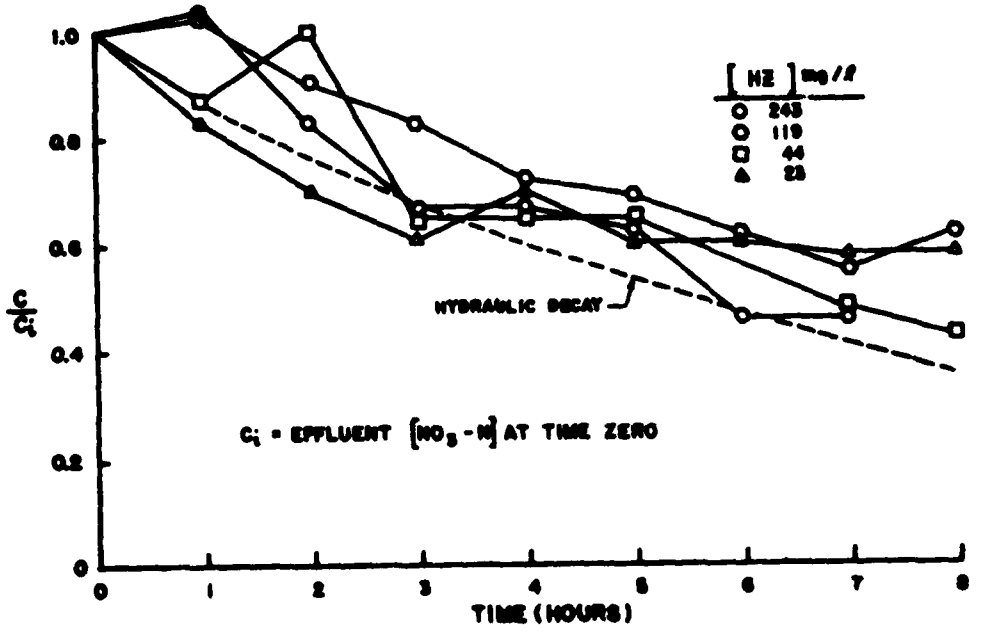


Figure 22. Acute Effluent Nitrate Nitrogen Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

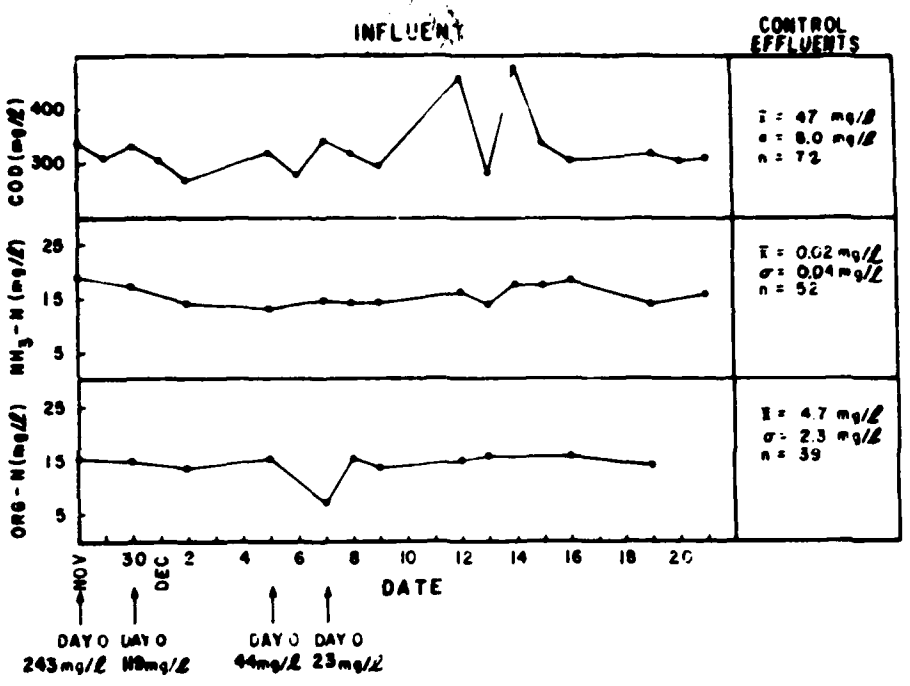


Figure 23. Influent and Control Effluent COD and Nitrogen Data During the Slug HZ Recovery Periods

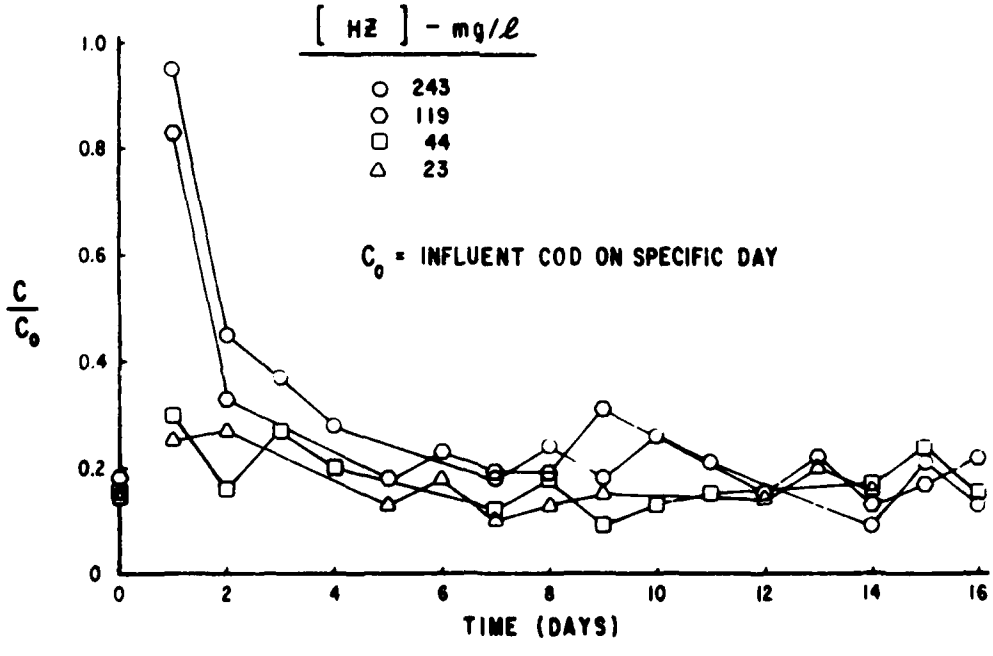


Figure 24. Effluent COD Recovery Following Slug HZ Loads (Mean of Duplicates)

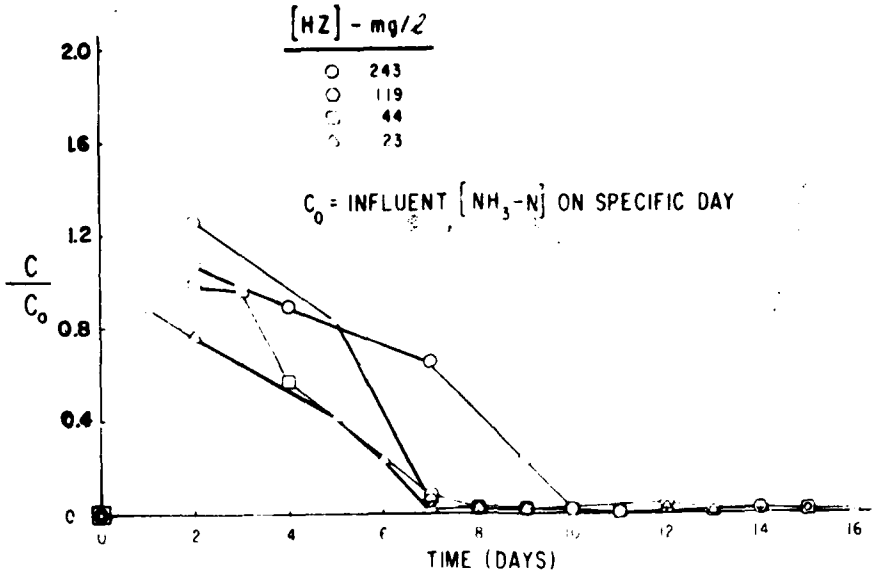


Figure 25. Effluent Ammonia Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates)

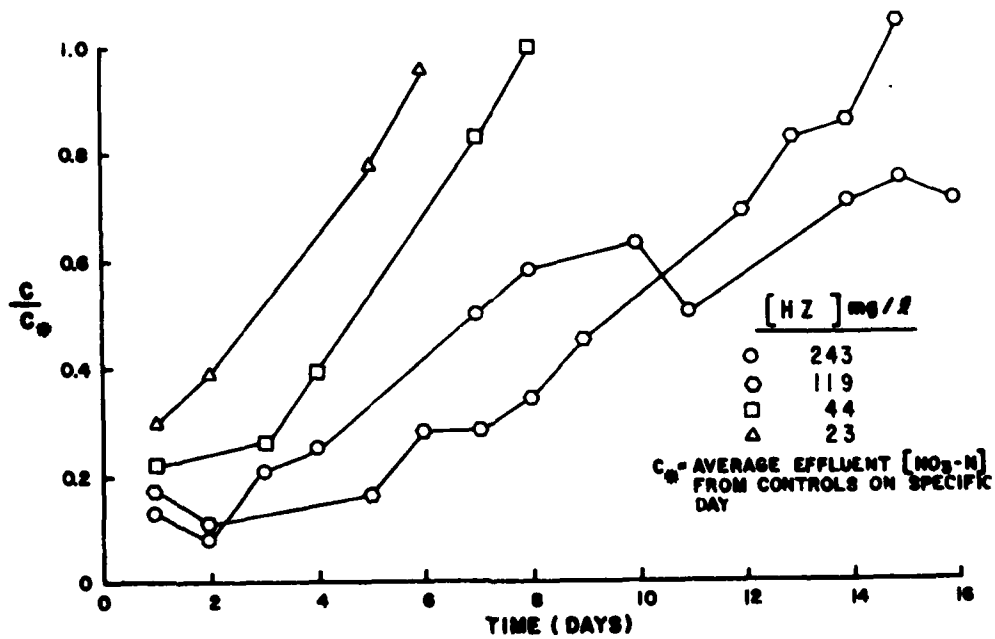


Figure 26. Effluent Nitrate Nitrogen Recovery Following Slug HZ Loads (Mean of Duplicates)

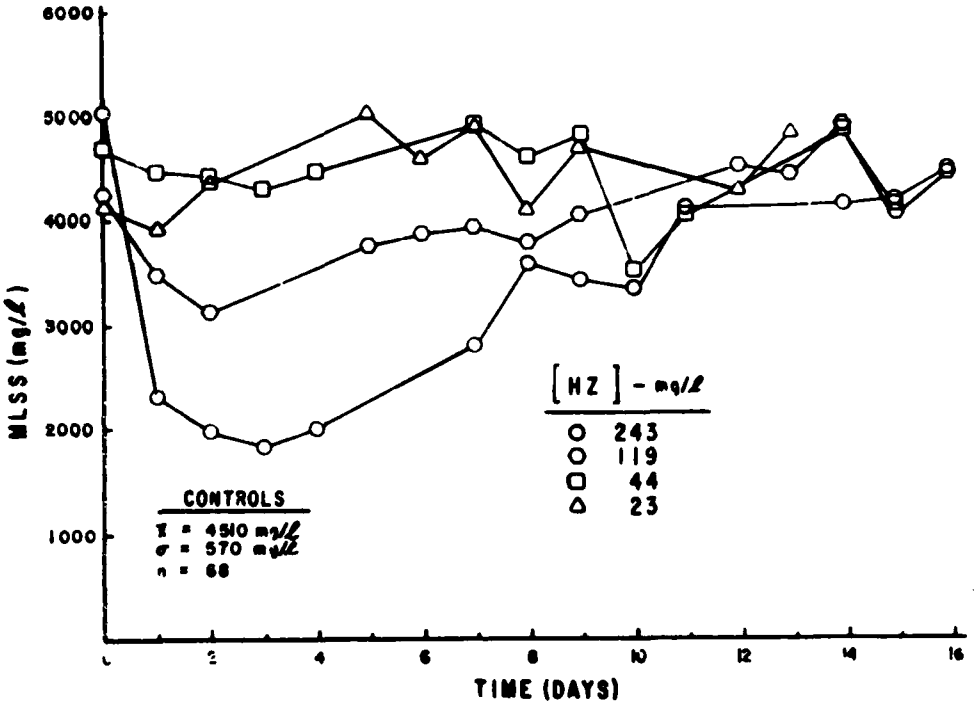


Figure 27. MLSS Response to Slug HZ Loads as a Function of Time (Mean of Duplicates)

SECTION V

RESULTS - MONOMETHYLHYDRAZINE (MMH)

Monomethylhydrazine is a colorless liquid with a density of 0.874 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125 mg/ℓ stock solution resulted in 1.56 mg COD/mg MMH, 0.03 mg NH_3-N/ mg MMH, and no detectable organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. MMH Degradation: Figure 28 shows the measured influent MMH concentrations during these studies. The theoretical and measured average influent and effluent MMH concentrations are summarized in Table 15.

As for HZ, control reactors with aerated tap water showed no MMH degradation over 8 hours. The percent reductions indicate microbial degradation or degradation catalyzed by the solids in the reactor. The low percent removal observed during the 0.5 mg/ℓ study (60 percent) is attributed to certain operational problems. During the 1/0.5 run effluent COD concentrations in the 0.5 mg/ℓ reactors rose significantly on day 3. Effluent organic-N values were not recorded on day 3 but were very high on day 4. COD, Organic-N, and NH_3-N values remained slightly elevated throughout the remainder of the study while MLSS concentrations declined One of the four reactors began to bulk significantly during this period.* It was also noted that the effluent quality of the controls was below normal with respect to both COD removal and nitrification during this time period; one control began to bulk on day 4*. It should be pointed out that all of the effluent parameters were extremely sensitive to bulking conditions: either directly (COD, org-N), owing to the filtration protocol (Whatman #40), or indirectly (NH_3-N, NO_3-N), as a result of decreased Θ_c. The above and the fact that the heterotrophic response seemed to be on the same order of magnitude as that for the autotrophs (uncharacteristic for these fuels), might suggest a transient hydraulic anomaly in reactors 5 to 12 as the cause for these observations. The reduced MMH degradation is assumed to be primarily a function of the decreased solids level.

Assuming that the average MMH degradation level at concentrations below 1 mg/ℓ is approximately 90 percent and 50 percent at 3 to 6 mg/ℓ, it is difficult to explain the 75-percent removal rate at 10 to 20 mg/ℓ. No explanation is offered at this time.

b. COD: The influent and control reactor effluent data are given in Table 16. Figure 29 shows the daily influent data as well as the mean effluent CODs from the four control reactors. Effluent quality in these reactors was clearly very stable. The high influent COD on day 1 for the 20/10 appears to be due to an unrepresentative sample (suspended matter) as the filtered sample had a COD of only 298 mg/ℓ.

*All effluent data from the 2 bulking reactors were ignored after day 4.

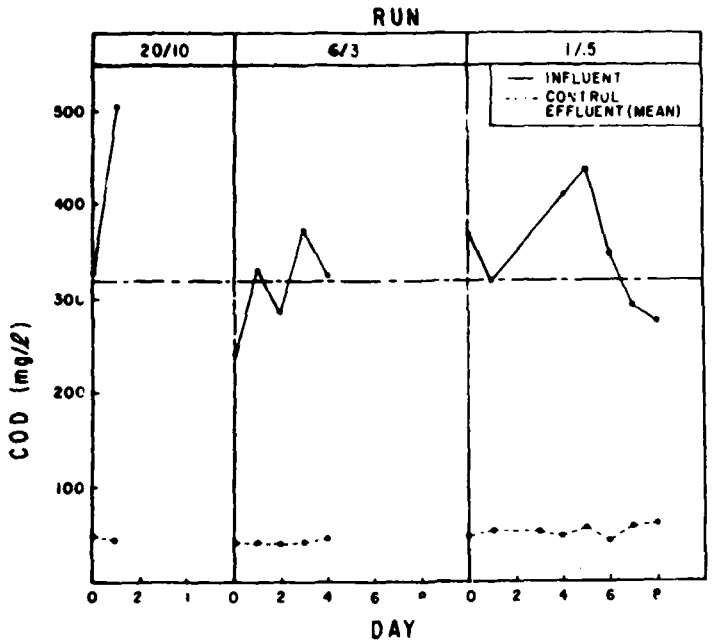


Figure 28. Continuous Feed Influent MMH Concentrations

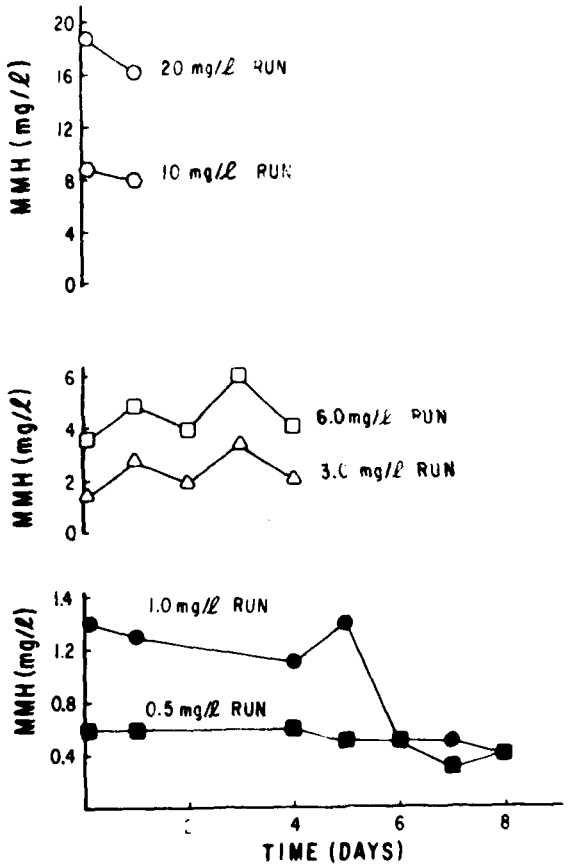


Figure 29. Influent COD and Mean Control Effluent COD Values During Continuous Feed MMH Runs

TABLE 15. MMH CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/ℓ)

Theoretical	Study Designation	Influent Mean	Influent σ	Influent n	Effluent Mean	Effluent σ	Effluent n	Reduction (Percent)
20	20/10	17.6	1.5	8	3.7	1.2	12	79
10	20/10	8.3	0.7	8	2.3	0.3	12	72
6.0	6/3	4.6	1.0	32	2.6	0.8	32	43
3.0	6/3	2.4	0.8	32	1.1	0.4	32	54
1.0	1/0.5	0.9	0.45	25	0.11	0.19	24	89
0.5	1/0.5	0.5	0.28	24	0.24	0.21	19	60

TABLE 16. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/ℓ) Mean	Influent COD (mg/ℓ) σ	Control Effluent COD (mg/ℓ) Mean	Control Effluent COD (mg/ℓ) σ	Control Percent Removal
20/10	1	417	125	48	3	88
6/3	4	312	51	43	4	86
1/0.5	8	352	60	54	12	85
Overall	-	347*	70	49**	10	86

* n = 14
**n = 56

TABLE 17. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/ℓ)

		INFLUENT				CONTROL EFFLUENT				
	Study Length	NH_3-N		TKN		NH_3-N		NO_3-N		Nitrification*
Study	(Days)	Mean	σ	Mean	σ	Mean	σ	Mean	σ	Percent in Control
20/10	1	12.2	0.6	44.1	24.3	0.0	0.0	31	1.0	70
6/5	4	11.8	2.1	29.8	2.9	0.0	0.0	27	2.0	91
11.5	8	8.3	1.2	27.8	9.8	0.3	1.3	19	3.8	68
Overall	-	10.1	2.4	31.0	11.6	0.2	0.9	25	5.4	81

*Based on TKN conversion to NO_3-N

Effluent COD as a function of influent MMH concentration and time is shown in Figure 30. Effluent quality was affected for all concentrations except 0.9 mg/ℓ. Increased DODs for the 0.5 mg/ℓ run after day 1 are unexplainable when compared with the 0.9 mg/ℓ data. Although pumping rates were checked on days 2 and 3, influent MMH concentrations were not quantified. It is possible that at some time during day 2 or day 3 a transient hydraulic anomaly caused elevated influent MMH concentrations which resulted in these high data points. This same trend was observed for organic nitrogen, as shown in Figure 31. A close correlation exists between effluent COD and organic nitrogen, as observed for HZ.

c. Nitrification: Influent and control effluent nitrogen data collected over the continuous feed MMH studies are outlined in Table 17. Overall, 81-percent nitrification of influent TKN was achieved.

The daily influent and control effluent parameters have been graphically displayed in Figures 32 and 34 for comparison with the data presented in Figure 33. Figure 33 indicates that the autotrophs are sensitive to MMH at concentrations above 0.5 mg/ℓ . The rising NH_3-N trend for the 0.5 mg/ℓ study after the 5-day point can be attributed to the high influent TKN on that day (Figure 32). The nitrate data in Figures 34 and 35 support this argument because, if the increased effluent ammonia concentrations were the result of MMH inhibition, nitrate concentrations would be expected to decline. Indeed, nitrate levels significantly increased in the control reactors. The nitrogen data contradicts the theory that hydraulic anomalies were responsible for elevated COD and organic nitrogen concentrations in the 0.5 mg/ℓ study. The 0.9 mg/ℓ plots in Figures 30 and 35 clearly show that the autotrophs are inhibited at this MMH concentration while the heterotrophs are not. MMH addition should not be expected to adversely affect COD and organic nitrogen with a concurrent rise in effluent NO_3-N. There remains no basis for the reduced COD removal observed for 0.5 mg/ℓ shown in Figure 30.

d. Suspended Solids: Table 18 summarizes the control suspended solids data. MLSS response to MMH is recorded in Figure 36. No difficulty was experienced in holding MLSS concentrations at the desired 4500 mg/ℓ even though it was qualitatively observed that effluent suspended solids increased during MMH feeds. The same dispersed fine floc was present as for the HZ runs, indicating cell lysis rather than a bulking mechanism as the cause.

TABLE 18. CONTROL MLSS DATA (mg/ℓ)

Study	Mean	σ	n
20/10	4710	277	8
6/3	4600	413	20
1/0.5	4600	508	24
Overall	4620	440	52

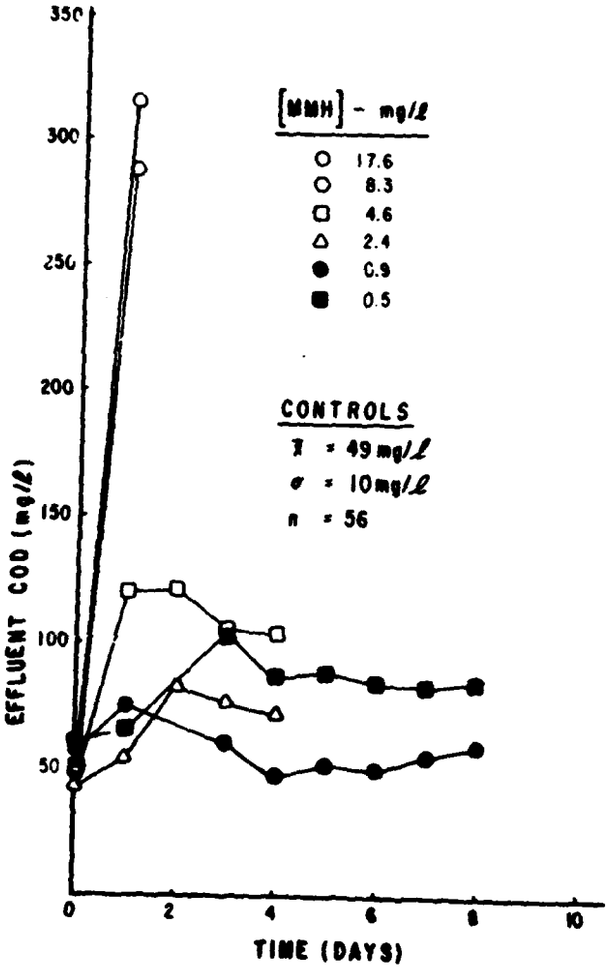


Figure 30. Effluent COD as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

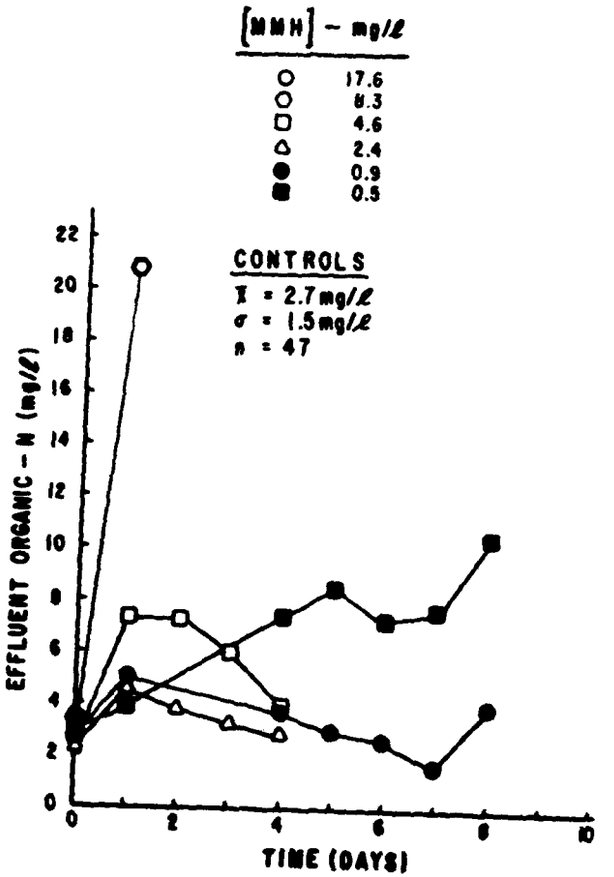


Figure 31. Effluent Organic Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

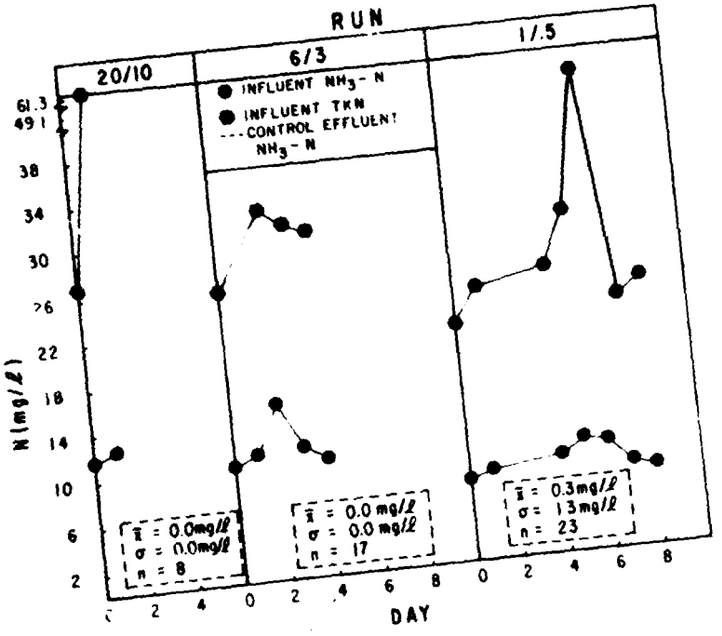


Figure 32. Influent and Control Effluent Nitrogen Data During Continuous Feed MMH Runs

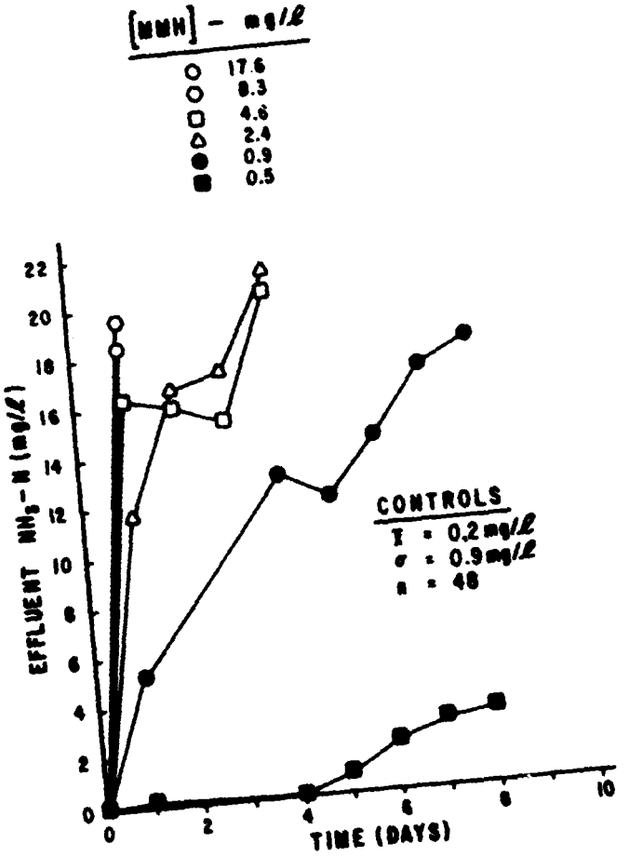


Figure 33. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

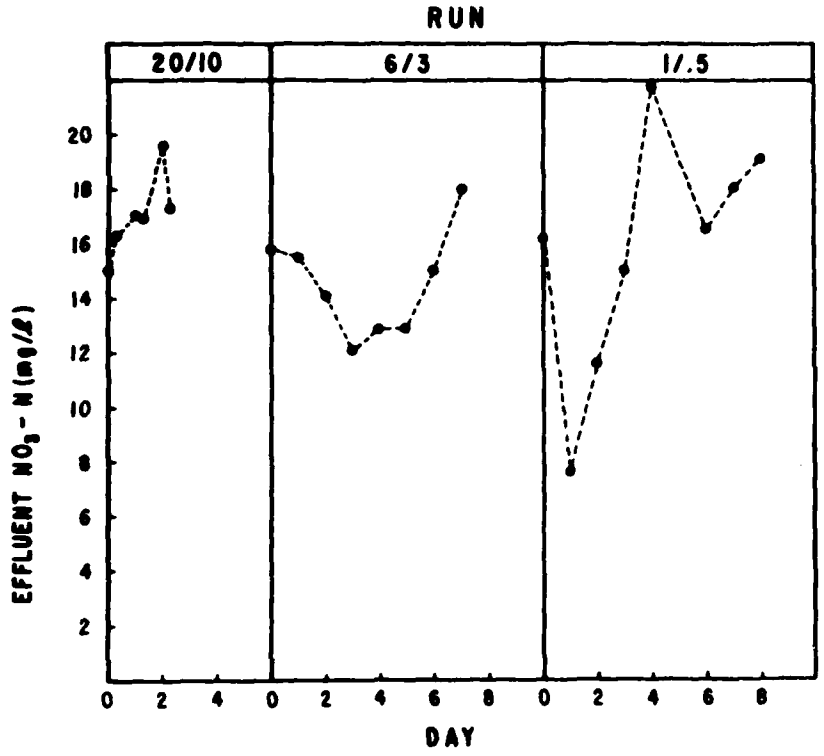


Figure 34. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed MMH Runs

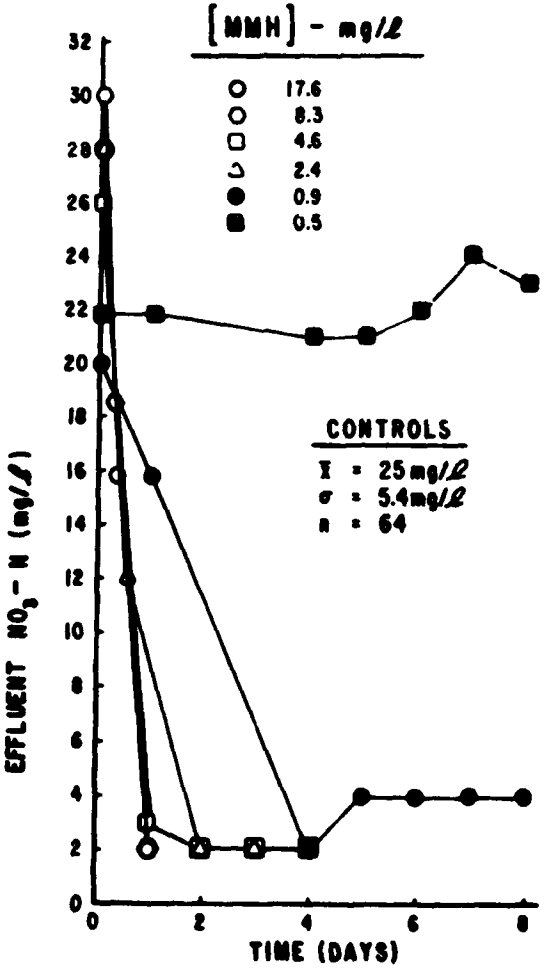


Figure 35. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed MMH Concentration (Mean of 4 Replicates)

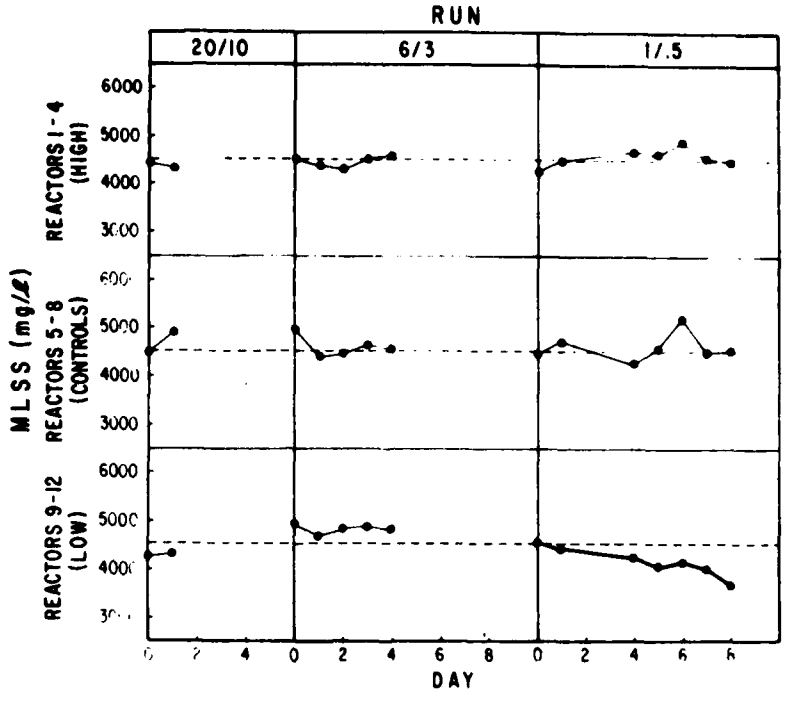


Figure 36. Mean MLSS During Continuous Feed MMH Runs (Mean of 4 Replicates)

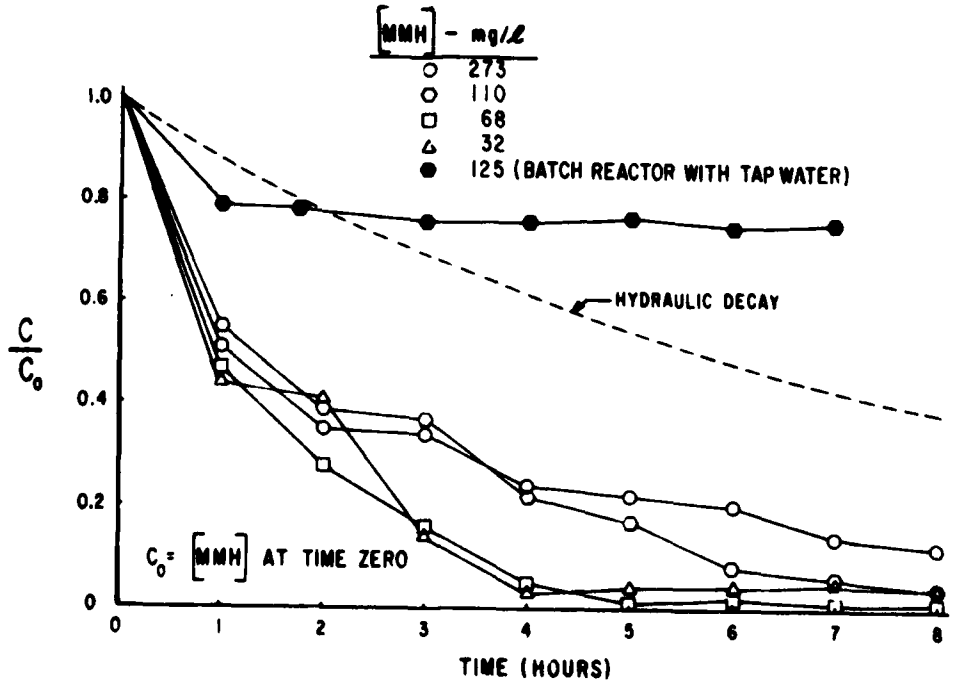


Figure 37. MMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)

2. SLUG FEED STUDIES

a. MMH Degradation: Figure 37 clearly shows that MMH was degraded during the slug feed experiments. Using Equation (25) the bacterial decay constants in Table 19 were derived. Figure 38 is a plot of the calculated half life ($t_{\frac{1}{2}}$) for MMH at each initial concentration.

TABLE 19. BACTERIAL DECAY CONSTANTS FOR MMH

Initial MMH (mg/ℓ)	$K(HR^{-1})$	Correlation Coefficient
32	0.293	0.7643
68	0.505	0.9160
110	0.262	0.9811
273	0.103	0.9324

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 20.

TABLE 20. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/ ℓ)

MMH		Influent			MLSS	
Theoretical	Measured	COD	NH_3-N	ORG-N	Mean	σ
250	273	391	10.9	13.8	4690*	78
125	110	391	10.9	13.8	4670*	71
50	68	382	9.0	20.2	4770*	516
25	32	382	9.0	20.2	4510	78

*Wasted to 4500 mg/l prior to slug

(1) COD: Figure 39 shows that effluent COD is effected at all slug MMH concentrations except 32 mg/ℓ. Figure 40 shows that the organic nitrogen response at 32 mg/ℓ MMH is initially much greater than for the 110 mg/ℓ and 68 mg/ℓ doses. These data are not understood. It can be shown that at the one hour point, for the 273 mg/ℓ slug, only 50 percent of the effluent COD was due to residual MMH in the reactor, indicating that cell lysis and/or metabolic inhibition had already occurred. This same data point in Figure 40 indicates that soluble organic nitrogen had been released in significant amounts at this time.

(2) Nitrification: The effect of MMH slug feeds on nitrification is shown in Figures 41 and 42. Even at 32 mg/ℓ there is complete inhibition after 8 hours. The nitrate decay rate is somewhat faster than that predicted based soley on hydraulics. The scatter in the individual concentration plots also suggests that some interference which results in decreased NO_3-N is a function of MMH concentration. This interference could not be duplicated in distilled water solutions and is unexplained.

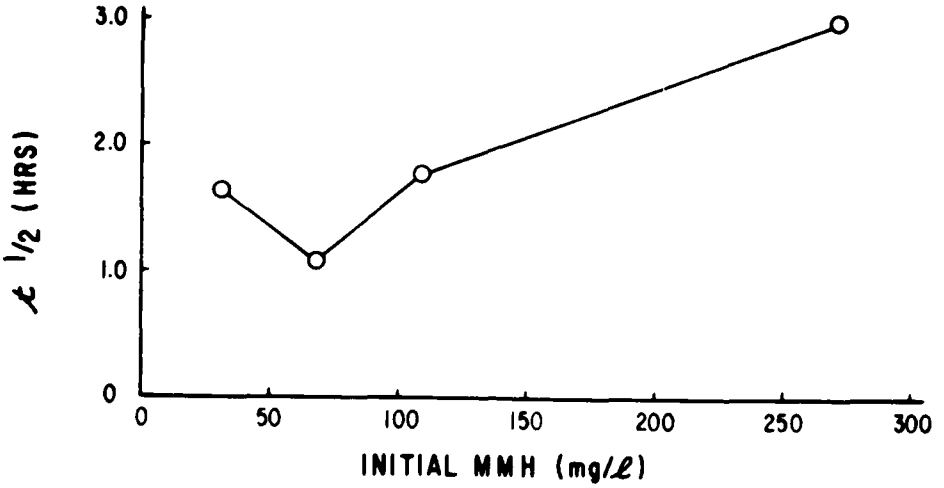


Figure 38. Calculated Halflife for MMH as a Function of Initial MMH Slug Concentration

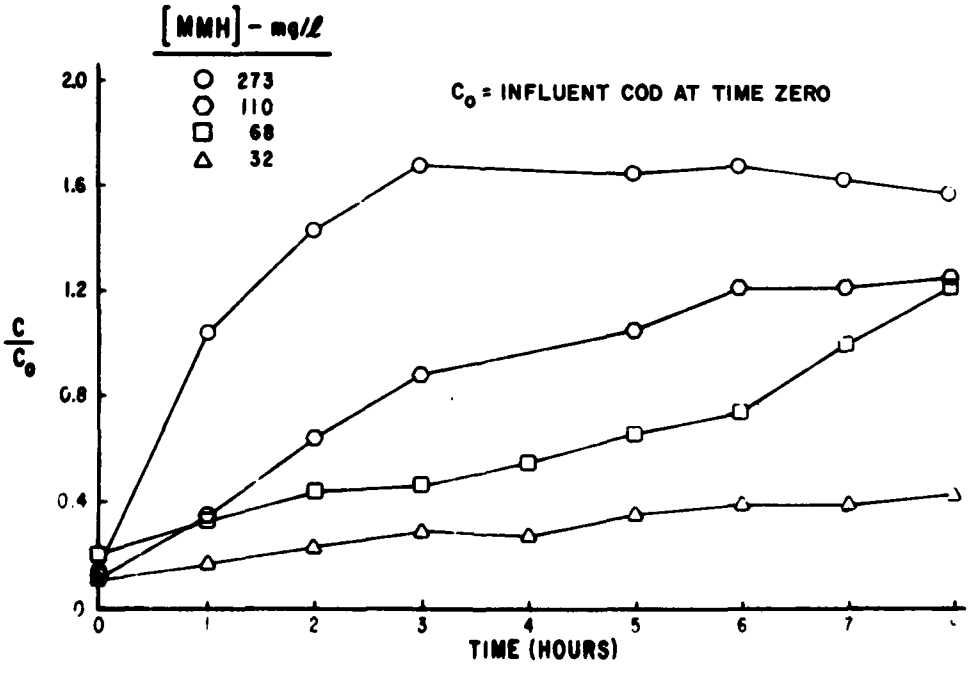


Figure 39. Actue Effluent COD Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

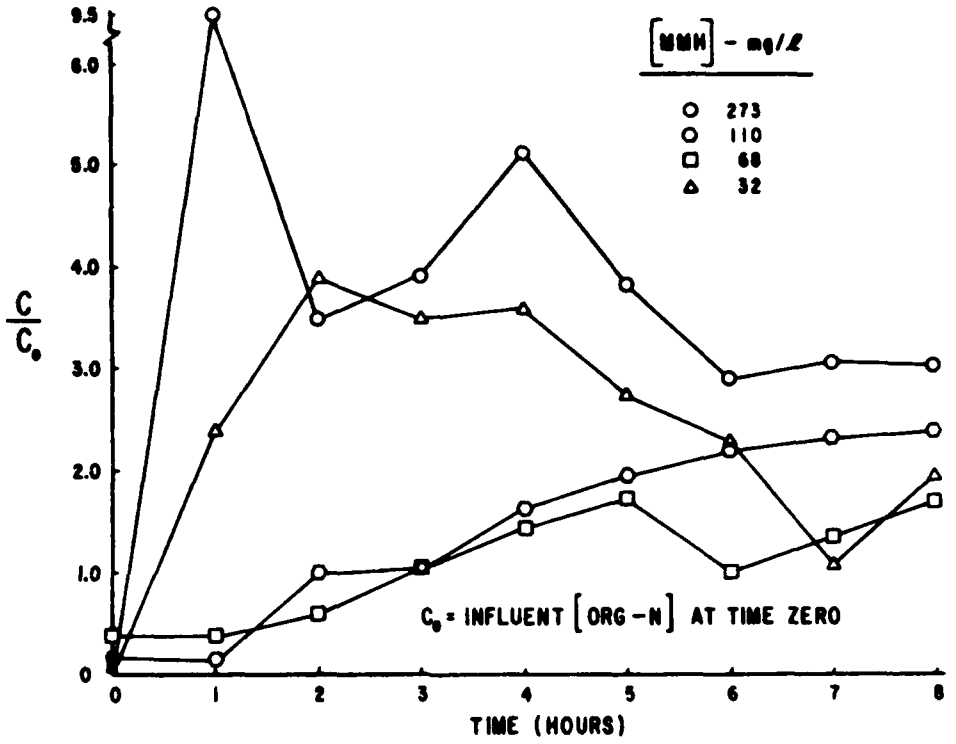


Figure 40. Acute Effluent Organic Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

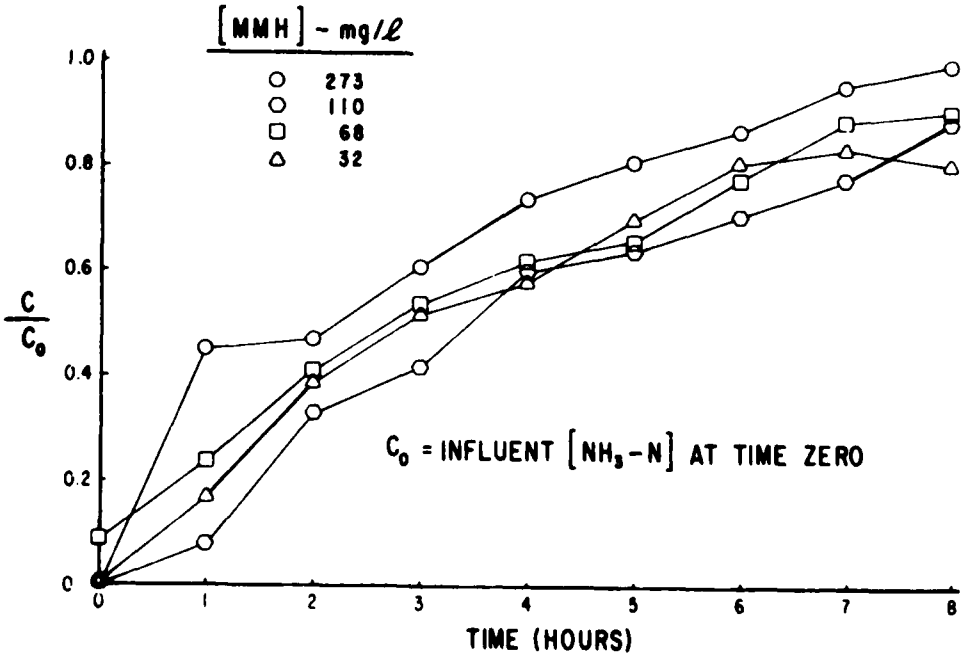


Figure 41. Acute Effluent Ammonia Nitrogen Response to Slug MMH Loads as a Function of Time (Mean) of Duplicates)

c. Recovery: The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 43.

(1) COD: Figure 44 illustrates that there was significant recovery within 3 days even for the 273 mg/ℓ slug.

(2) Nitrification: Recovery of the nitrifying bacteria is slower than for the heterotrophs. In Figure 45, it can be seen that 12 to 16 days were required to return effluent ammonia levels to their pre-exposure level. Figure 46 is a plot of effluent nitrate recovery for the MMH study. As no control data was available from days 6 and 8 on for the 68/32 mg/ℓ and 273/110 mg/ℓ slugs, respectively, a plot of actual effluent NO_3-N versus time for this period has been presented as an inset. While this does not represent recovery as well as the comparison with control effluent NO_3-N (C/C_*), the rising trend in nitrite oxidation is dramatic enough to make inferences about nitrate recovery. The data suggest that approximately 16 days are required for complete recovery. The lag observed in establishing a Nitrobacter sp population during the HZ study appears to have been reproduced in the MMH study although overall MMH recovery periods were longer by 4 to 6 days.

(3) Suspended Solids: The MLSS response to MMH as shown in Figure 47 was not as drastic as for comparable HZ concentrations even though the COD and organic nitrogen effects were similar in magnitude. MLSS values never dropped below 3200 mg/ℓ, returning to normal levels in all cases after 4 days. The decline in MLSS for the 68 mg/ℓ and 32 mg/ℓ studies after day 7 is attributed to bulking in 3 out of the 4 reactors (10, 11, 12) and not MMH. The reason for the bulking in these specific reactors is not known but is assumed to be related to hydraulic anomalies as this problem was noted from time to time in different reactors (including controls) but generally not in all 12 at once.

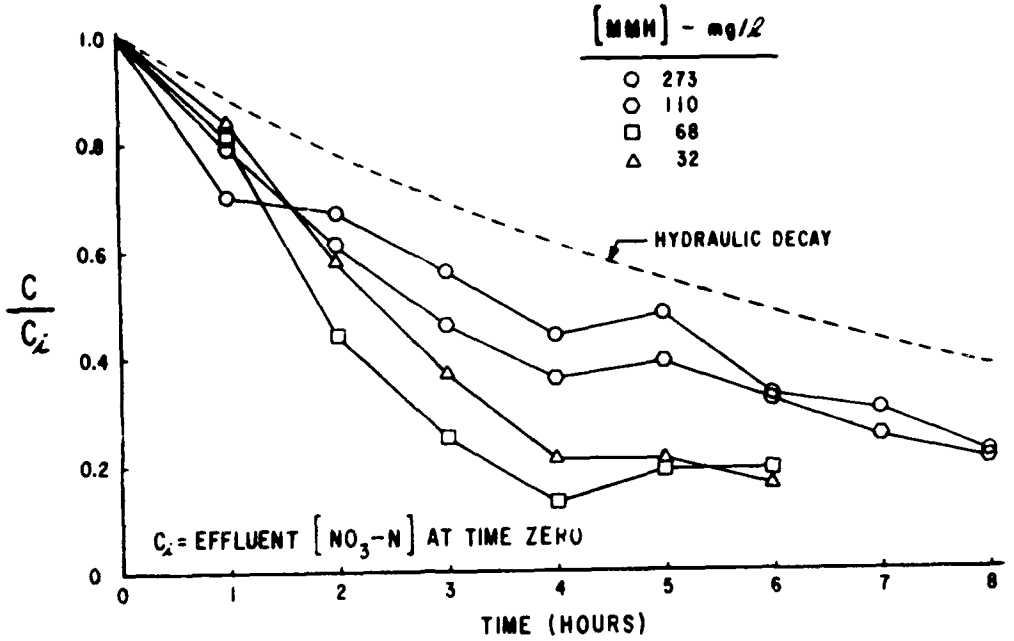


Figure 42. Acute Effluent Nitrate Nitrogen Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

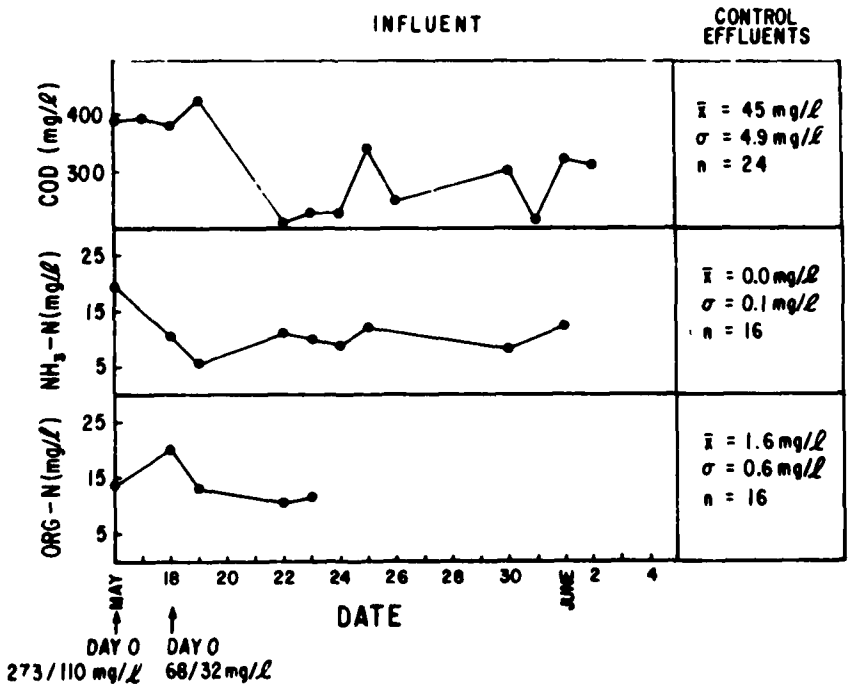


Figure 43. Influent and Control Effluent COD and Nitrogen Data During the Slug MMH Recovery Periods

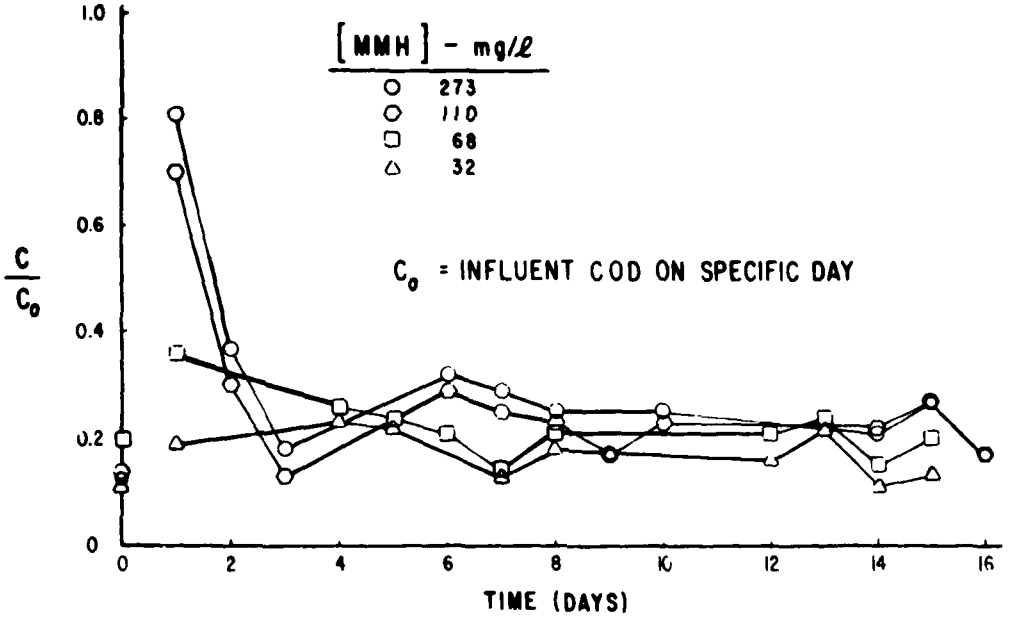


Figure 44. Effluent COD Recovery Following Slug MMH Loads (Mean of Duplicates)

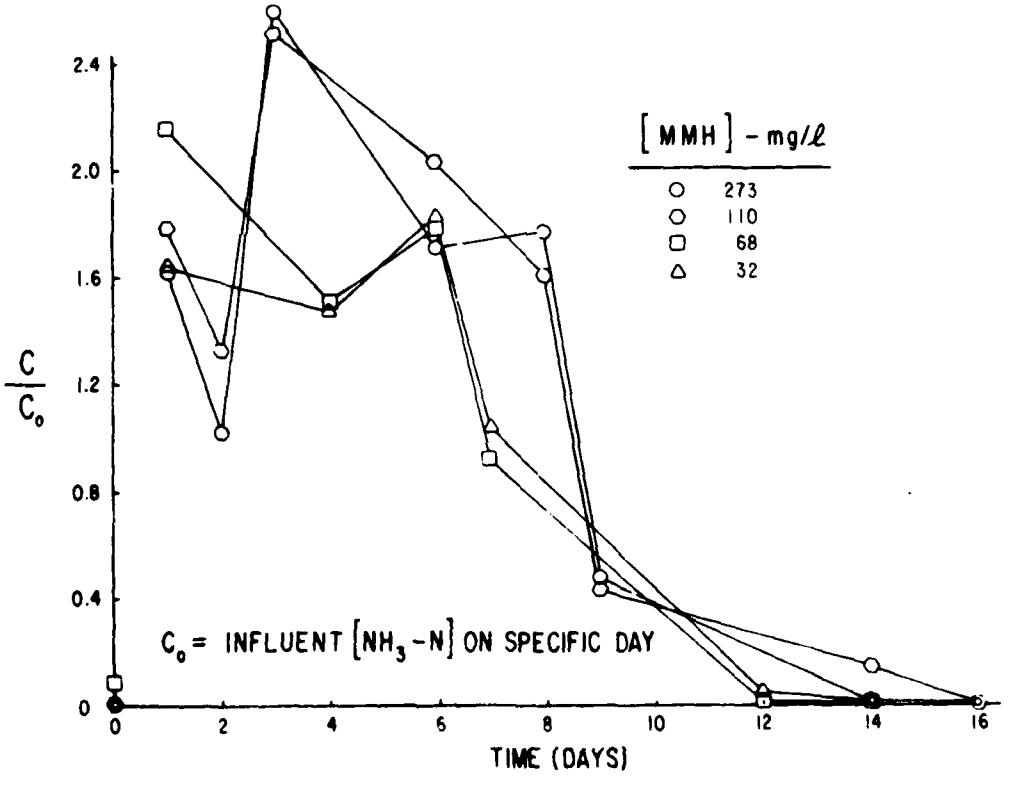


Figure 45. Effluent Ammonia Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates)

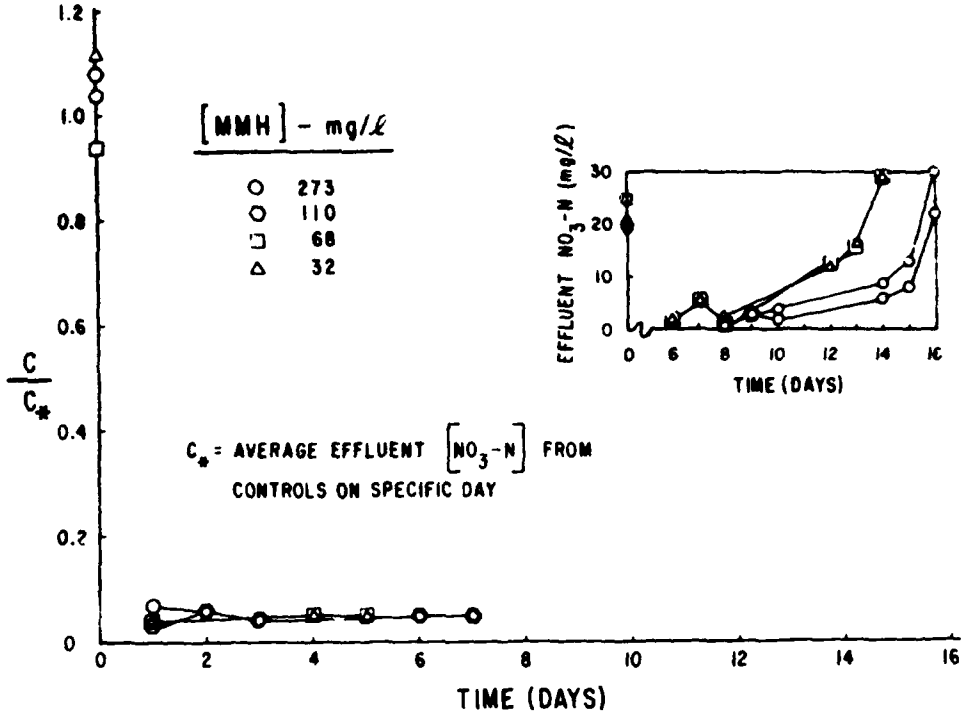


Figure 46. Effluent Nitrate Nitrogen Recovery Following Slug MMH Loads (Mean of Duplicates)

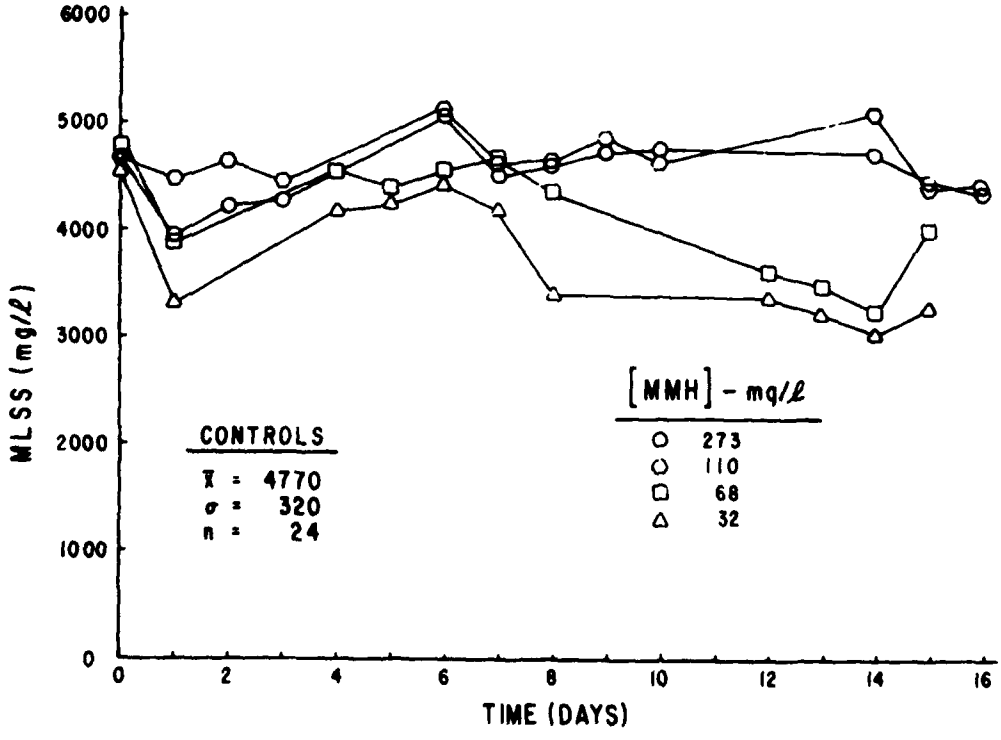


Figure 47. MLSS Response to Slug MMH Loads as a Function of Time (Mean of Duplicates)

SECTION VI

RESULTS - UNSYMMETRICAL DIATHYLHYDRAZINE (UDMH)

Unsymmetrical dimethylhydrazine is a colorless liquid with a density of 0.786 gm/ml at 20°C. It is very soluble in water. Duplicate analyses of a 125 mg/ℓ stock solution resulted in 1.89 mg COD/mg UDMH, 0.15 mg NH_3-N/mg UDMH, and no detectable organic nitrogen.

1. CONTINUOUS FEED STUDIES

a. UDMH Degradation: The influent UDMH data are shown in Figure 48 and indicate some variation about the target concentrations. Each point represents the average of 4 reactors. The influent and effluent data have been summarized in Table 21.

While degradation occurs at all concentrations investigated, it is interesting to note that the percent reductions are significantly lower than for neat hydrazine at comparable concentrations. This will be addressed in more detail in the next section.

b. COD: Table 22 summarizes the influent and control reactor effluent data for the continuous feed studies.

Figure 49 shows the daily influent data as well as the mean effluent CODs from the four control reactors. Remaining COD in the clarifier effluent as a function of influent UDMH concentration and time is shown in Figure 50. When compared with the control data, it would seem that the no effect UDMH concentration is approximately 5 mg/ℓ. The response at 8.0 and 18.9 mg/ℓ is essentially the same but less than that documented for HZ and MMH by a factor of two for comparable concentrations. It would also appear as if some degree of acclimation occurred as the effluent CODs exhibited a steady downward trend after day 2. This information is extremely interesting in light of the UDMH degradation data presented later. Although the toxic effects appear to be significantly less than that observed for HZ and MMH, UDMH is degraded at one-half the rate. This would suggest that UDMH was serving as an alternate carbon source to which the heterotrophic organisms may acclimate after 4 to 5 days. The HZ molecule is similar to that of ammonia, NH_3, and it is theorized that HZ is taken into the cell by means of a like mechanism exhibiting its toxic effect once assimilated. This would account for the high degradation rate for HZ with high concurrent toxicity. The organic nitrogen data in Figure 51 also supports this argument as heterotrophic cell lysis, represented by effluent organic-N, was minimal.

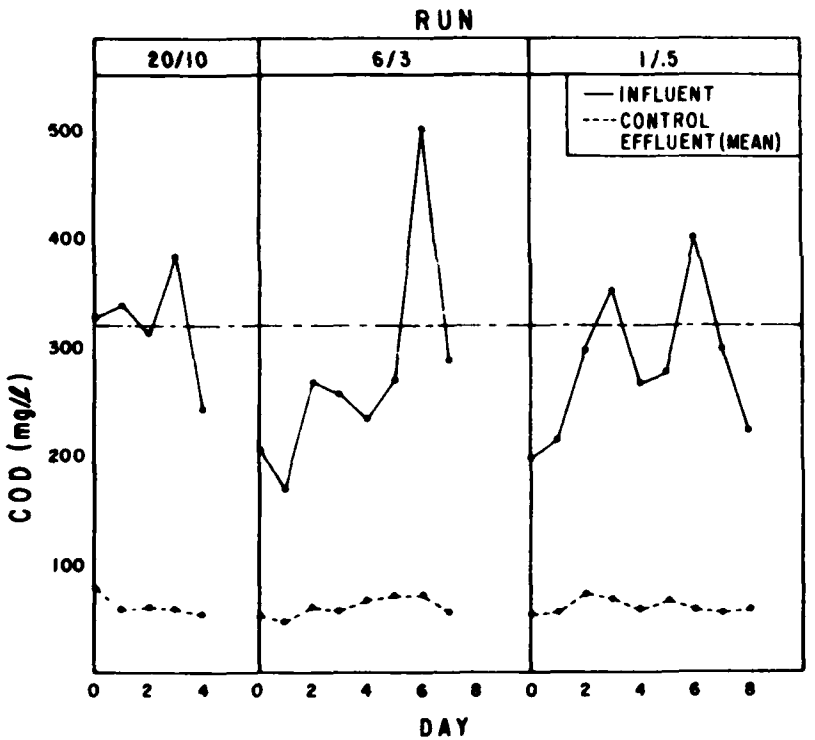


Figure 48. Continuous Feed Influent UDMH Concentrations

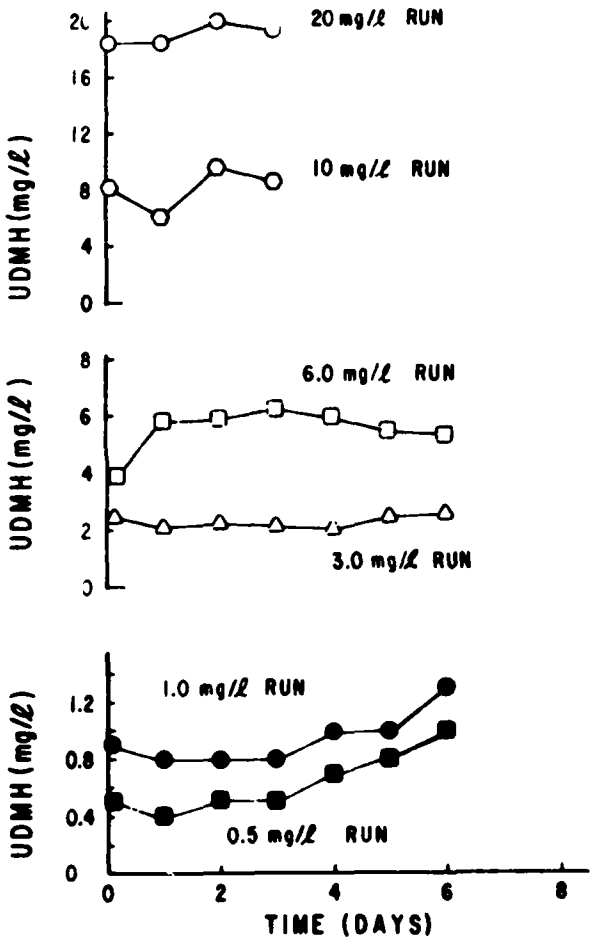


Figure 49. Influent COD and Mean Control Effluent COD Values During Continuous Feed UDMH Runs

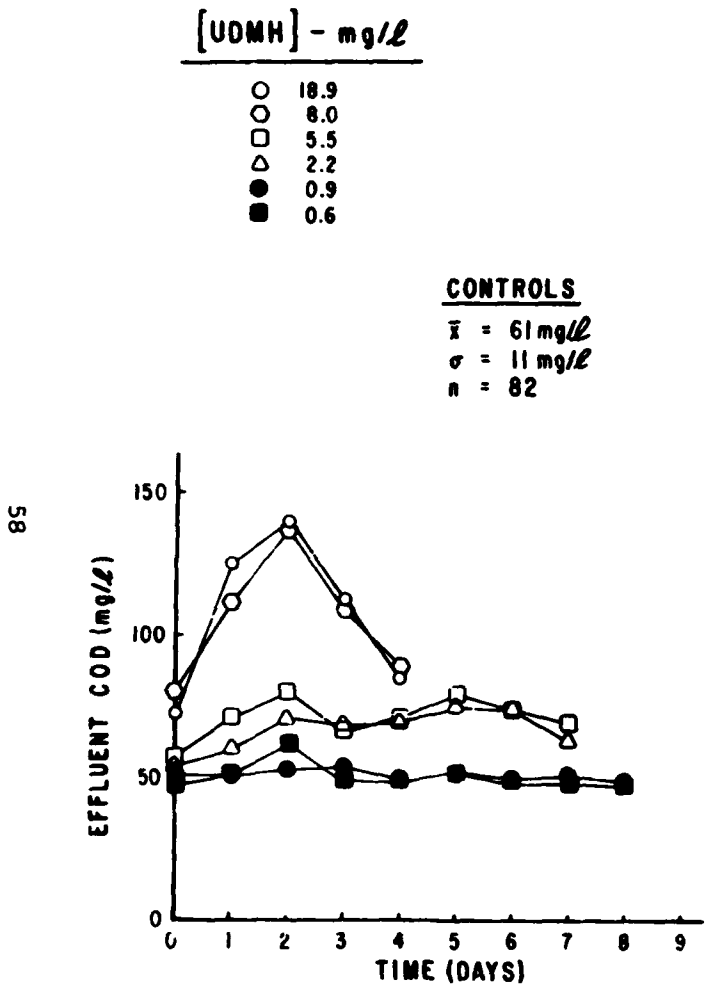


Figure 50. Effluent COD as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)

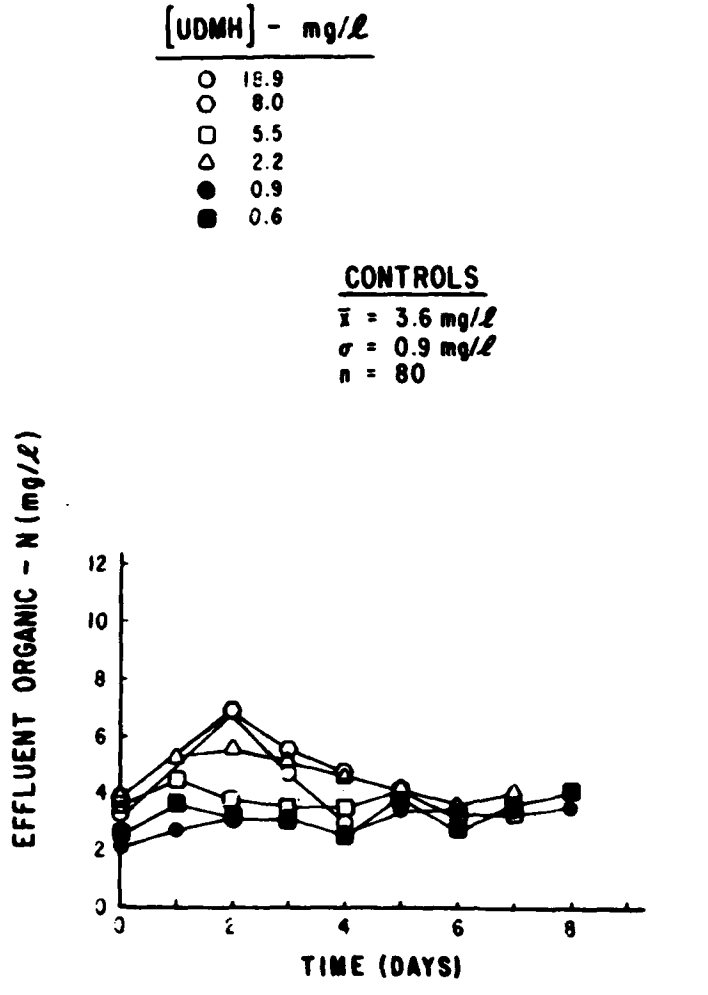


Figure 51. Effluent Organic Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates)

TABLE 21. UDMH CONCENTRATIONS DURING CONTINUOUS FEED STUDIES (mg/ℓ)

Theoretical	Study Designation	Influent Mean	Influent σ	Effluent Mean	Effluent σ	Reduction Percent
20	20/10	18.9	0.7	12.6	1.1	33
10	20/10	8.0	1.4	4.5	0.6	44
6.0	6/3	5.5	0.8	2.9	0.5	47
3.0	6/3	2.2	0.2	0.8	0.4	64
1.0	1/0.5	0.9	0.2	0.15	0.07	83
0.5	1/0.5	0.6	0.2	0.04	0.08	93

TABLE 22. INFLUENT AND CONTROL EFFLUENT COD SUMMARY

Study	Study Length (Days)	Influent COD (mg/ℓ) Mean	Influent COD (mg/ℓ) σ	Control Effluent COD (mg/ℓ) Mean	Control Effluent COD (mg/ℓ) σ	Control Percent Removal
20/10	4	320	51	63	15	80
6/3	7	276	99	60	9	78
1/0.5	8	284	64	61	11	79
Overall	-	278*	87	61**	11	78

* n = 22
** n = 82

c. Nitrification: The influent and control effluent nitrogen data collected over the continuous feed UDMH studies are presented in Table 24.

The daily influent and control effluent parameters have been graphically displayed in Figures 52 and 54 for comparison with the daily effluent qualities in those reactors receiving UDMH. From Figure 53, it is apparent that concentrations above approximately 1 mg/ℓ cause inhibition of nitrification. The nitrate data presented in Figure 55 agree well with the ammonia data. The drop in effluent NO_3-N on day 1 was observed in the control reactors (Figure 54) as well as for the 0.9 and 0.6 mg/ℓ UDMH reactors. Unlike the heterotrophs, there appears to be no autotrophic acclimation to UDMH.

d. Suspended Solids: The suspended solids data for the control reactors are outlined in Table 23. Figure 56 summarizes all MLSS data.

TABLE 23. CONTROL MLSS DATA (mg/ℓ)

Study	Mean	σ	n
20/10	4710	360	15
6/3	4660	530	32
1/0.5	4630	460	36
Overall	4660	470	83

No difficulty was experienced in holding MLSS concentrations at the desired 4500 mg/ℓ. As noted earlier cell lysis, and hence effluent solids, was minimal during the UDMH studies.

TABLE 24. INFLUENT AND CONTROL EFFLUENT NITROGEN SUMMARY (mg/ℓ)

Study	Study Length (Days)	Influent NH_3-N Mean	Influent NH_3-N σ	Influent TKN Mean	Influent TKN σ	Control Effluent NH_3-N Mean	Control Effluent NH_3-N σ	Control Effluent NO_3-N Mean	Control Effluent NO_3-N σ	Nitrification* Percent in Controls
20/10	4	14.7	2.2	27.6	4.0	0.3	0.5	22	1.0	80
6/3	7	5.7	2.1	20.9	2.7	0.1	0.6	15	2.2	72
1/0.5	8	8.7	2.7	23.0	3.8	0.3	1.2	16	4.7	70
Overall	-	8.7	4.0	23.1	4.1	0.7	0.9	17	4.2	74

* Based on TKN conversion to NO_3-N

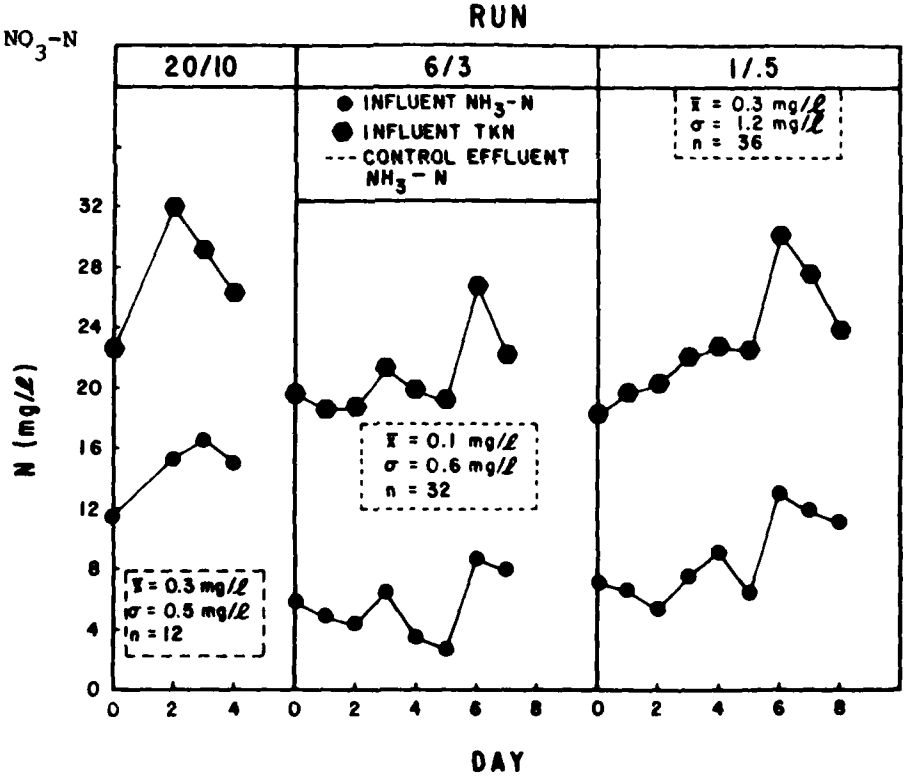


Figure 52. Influent and Control Effluent Nitrogen Data During Continuous Feed UDMH Runs

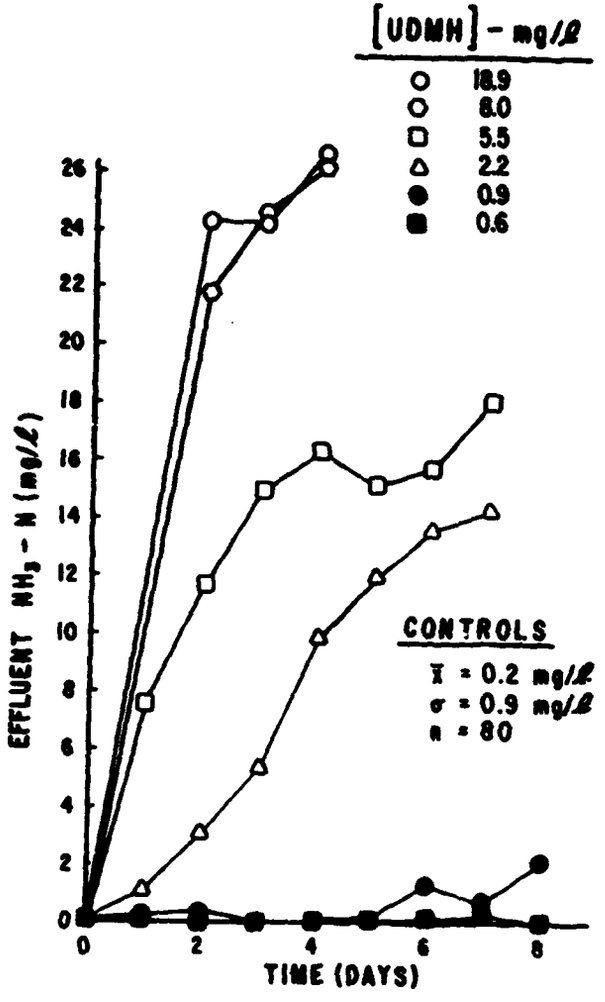


Figure 53. Effluent Ammonia Nitrogen as a Function of Time and Continuous Feed UDMH Concentration (Mean of 4 Replicates).

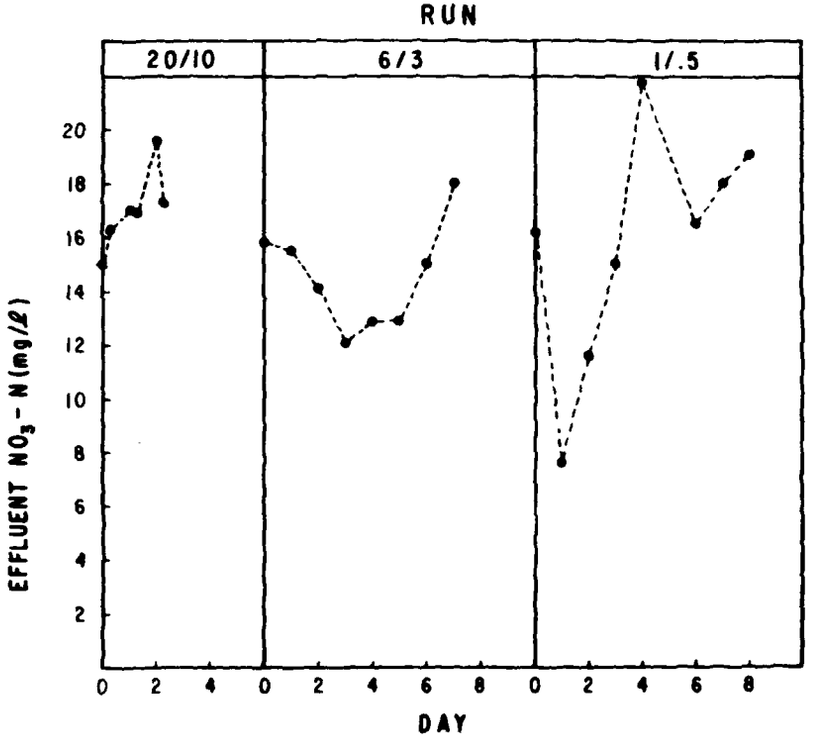


Figure 54. Mean Control Effluent Nitrate Nitrogen Values During Continuous Feed UDMH Runs.

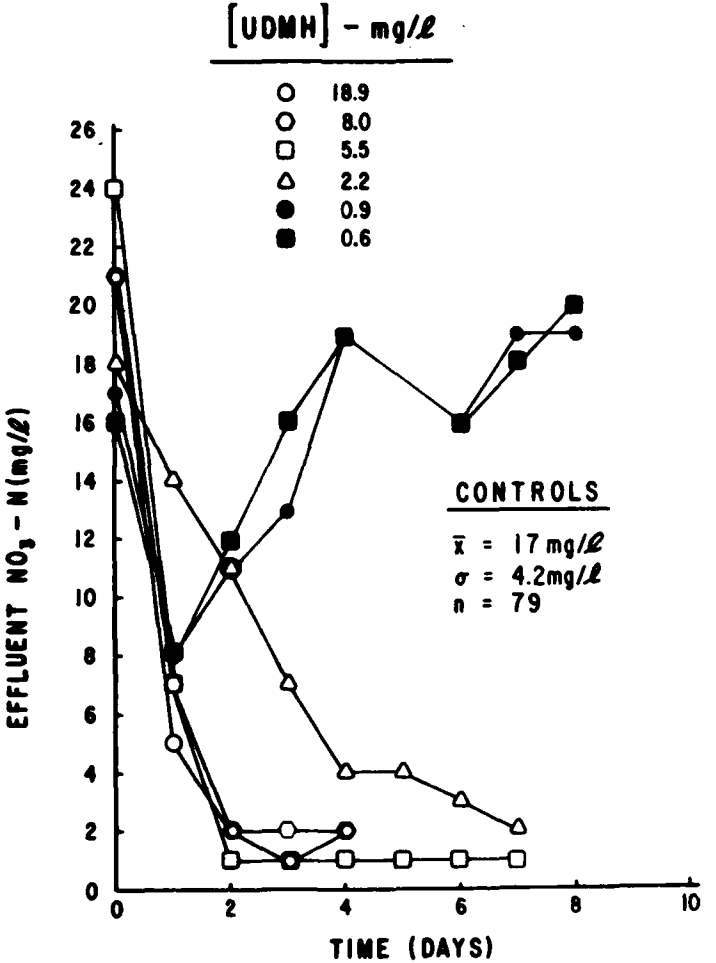


Figure 55. Effluent Nitrate Nitrogen as a Function of Time and Continuous Feed MDMH Concentration (Mean of 4 Replicates)

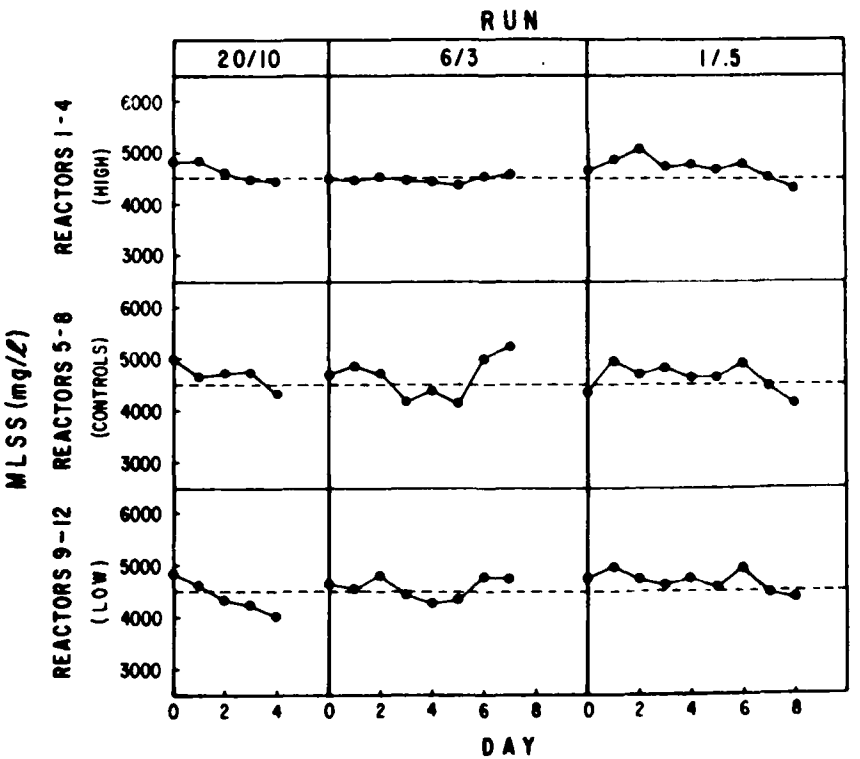


Figure 56. Mean MLSS During Continuous Feed UDMH Runs (Mean of 4 Replicates)

2. SLUG FEED STUDIES

a. UDMH Degradation: Figure 57 clearly shows that UDMH was degraded during the slug feed experiments but at a lower rate than for HZ or MMH. The bacterial decay constants and half lifes were computed as described earlier and are shown in Table 25 and Figure 58. These data agree well with the degradation theory proposed for the continuous feed results.

TABLE 25. BACTERIAL DECAY CONSTANTS FOR UDMH

Initial UDMH (mg/ℓ)	$K(HR^{-1})$	Correlation Coefficient
255	0.075	0.9754
128	0.053	0.9858
74	0.1192	0.9592
22	0.095	0.9827

b. Acute Response: Influent parameters during the 8-hour acute response study are summarized in Table 26 below.

TABLE 26. SLUG LOAD RESPONSE INITIAL CONDITIONS (mg/ℓ)

UDMH		Influent			MLSS	
Theoretical	Measured	COD	NH_3-N	ORG-N	Mean*	σ
250	255	226	10.0	11.6	4730	230
125	128	226	10.0	11.6	4800	40
50	74	336	12.2	18.3	5120	300
25	22	314	11.6	21.5	5170	400

*Wasted to 4500 mg/ℓ prior to slug

(1) COD: Figure 59 shows that effluent COD is not effected at slug doses below 74 mg/ℓ. At the two hour point approximately 84 percent of the effluent COD was due to residual UDMH in the reactor. The remainder, 57 mg/ℓ, representing no decline in substrate degradation. The organic nitrogen data in Figure 60 correlates well as it shows essentially no system upset even at 255 mg/ℓ UDMH. However, at 3 hours some 90 mg/ℓ of the effluent COD cannot be attributed to UDMH. Effluent organic nitrogen concentrations rose only slightly at this time, the implication being that the heterotrophic effects of slug UDMH doses in the range investigated are more related to inhibition than to toxicity and that these effects do not become manifest until approximately 3 hours post exposure. Concentrations below 74 mg/ℓ UDMH produced no adverse effect.

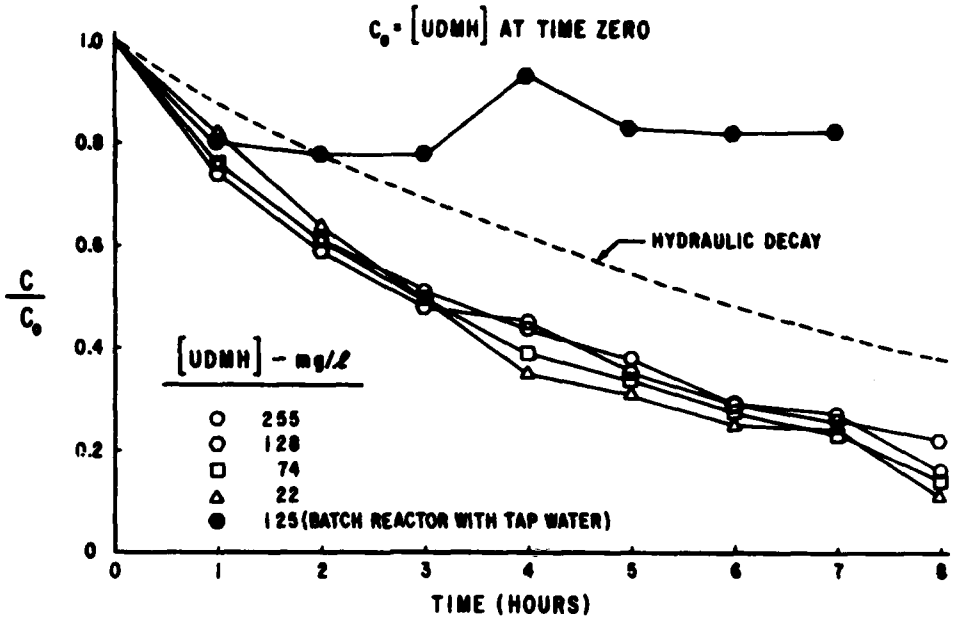


Figure 57. UDMH Degradation During MMH Slug Feed Experiments (Mean of Duplicates)

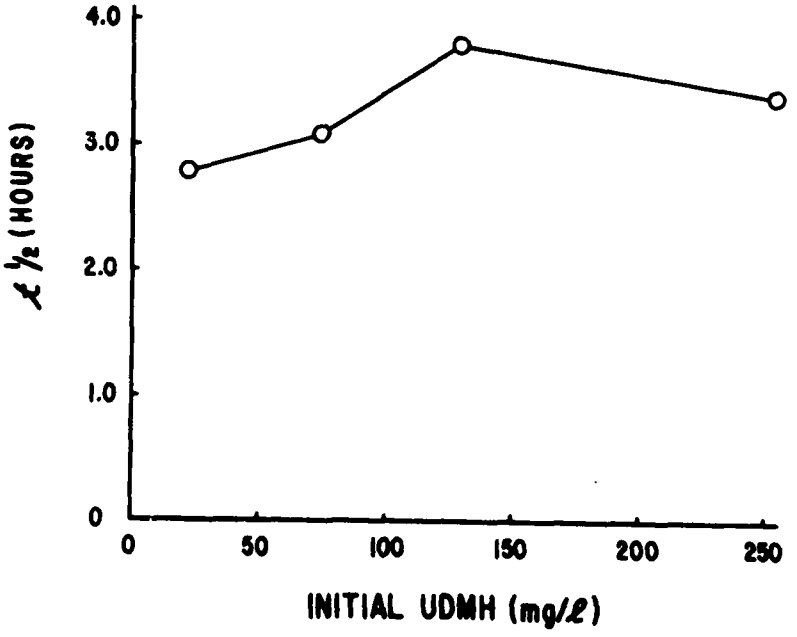


Figure 58. Calculated Halflife for MMH as a Function of Initial UDMH Slug Concentration

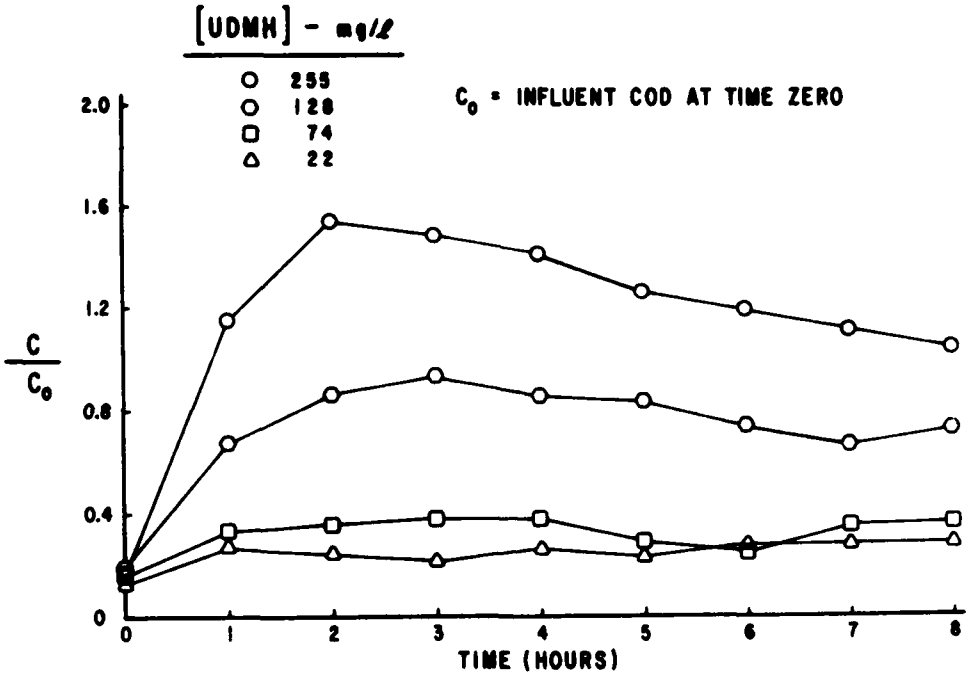


Figure 59. Acute Effluent COD Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

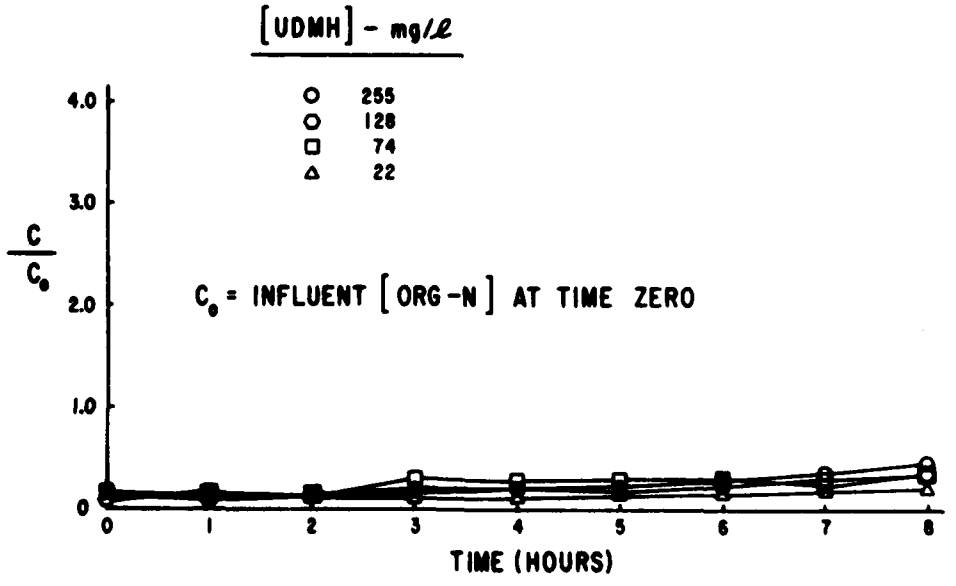


Figure 60. Acute Effluent Organic Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

(2) Nitrification: The effect of UDMH slug feeds on nitrification is shown in Figures 61 and 62. Even at 22 mg/ℓ, inhibition is complete after 8 hours. At 255 mg/ℓ, it can be shown that inhibition is complete at 2 hours post exposure. The nitrate decay rate is essentially equal to that expected for a completely mixed reactor with no influent nitrate, indicating that at all concentrations the oxidation of ammonia to nitrate has ceased. Note that all of the plots are slightly above the predicted decay curve, an observation which suggests that inhibition was not instantaneous. If time zero is taken at 1 hour, the hydraulic decay and 255 mg/ℓ curves are almost identical.

c. Recovery: The influent and control effluent COD and nitrogen data monitored throughout the recovery period are outlined in Figure 63.

(1) COD: Figure 64 indicates significant recovery after 48 hours for both the 255 mg/ℓ and 128 mg/ℓ slug feeds.

(2) Nitrification: Recovery of the nitrifying bacteria was again slower than for the heterotrophs. Figure 65 shows that 8 to 9 days were required to return to the pre-exposure ammonia oxidation levels. Effluent nitrate concentrations (Figure 66) are displayed as the slug reactor mean over the mean control value for all days except 0 to 9 during the 252 mg/ℓand 128 mg/ℓ studies. As no control data was available, a plot of actual effluent NO_3-N versus time has been presented as an inset. The nitrate recovery times match the ammonia recovery times very closely. This again implies that the autotrophic bacteria were inhibited rather than eliminated by the UDMH. No explanation can be offered with respect to the C/C_o values in excess of unity for NH_3-N. Note that this same phenomena occurred during the MMH slug studies.

(3) Suspended Solids: The MLSS response to UDMH was minimal, as shown in Figure 67. The low value on day 7 for the 255 mg/ℓ run was due to a low MLSS determination (2500 mg/ℓ). This anomaly was attributed to unrepresentative sampling noting that the MLSS was 4470 mg/ℓ the following day.

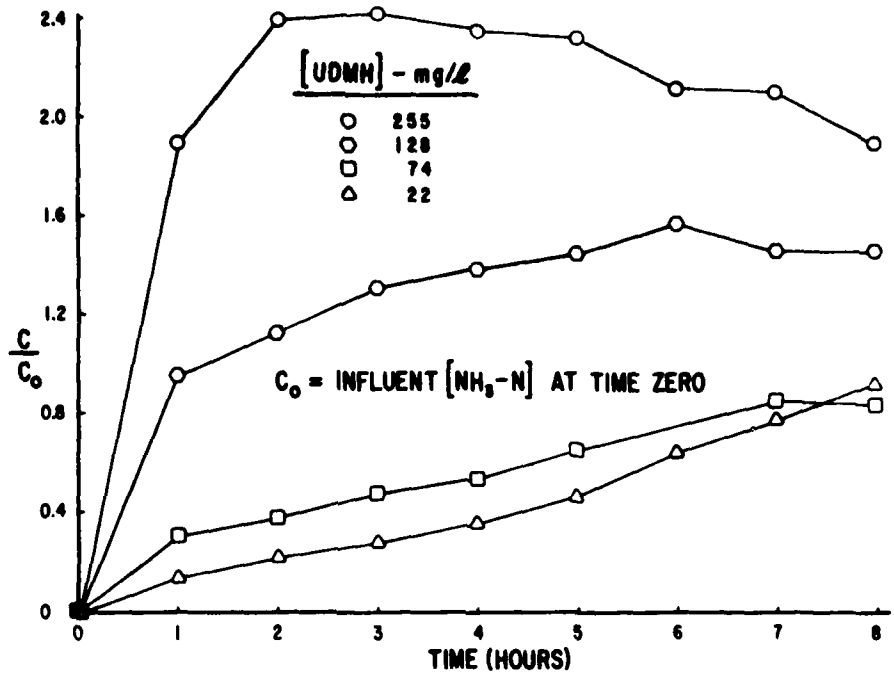


Figure 61. Acute Effluent Ammonia Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

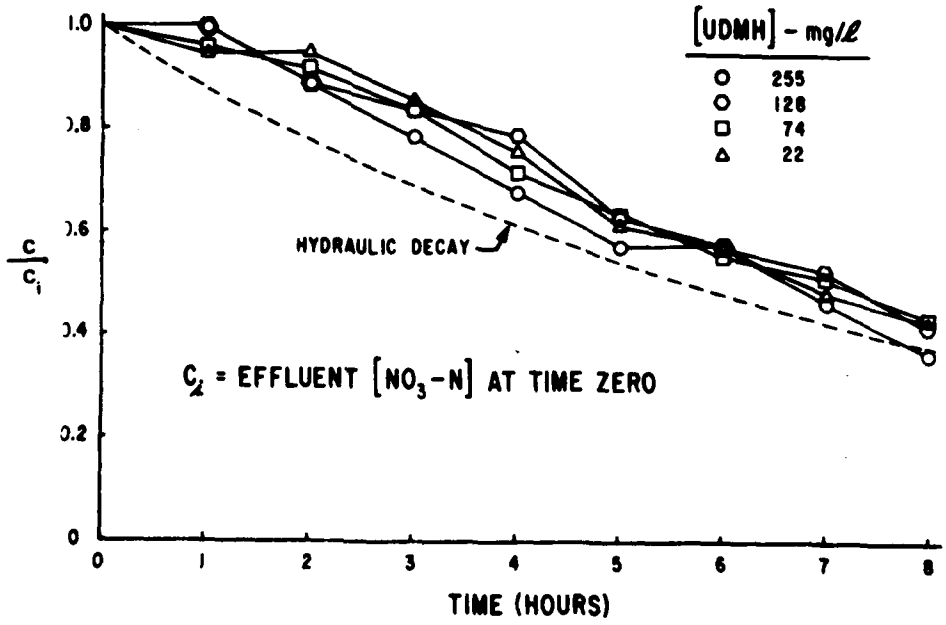


Figure 62. Acute Effluent Nitrate Nitrogen Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

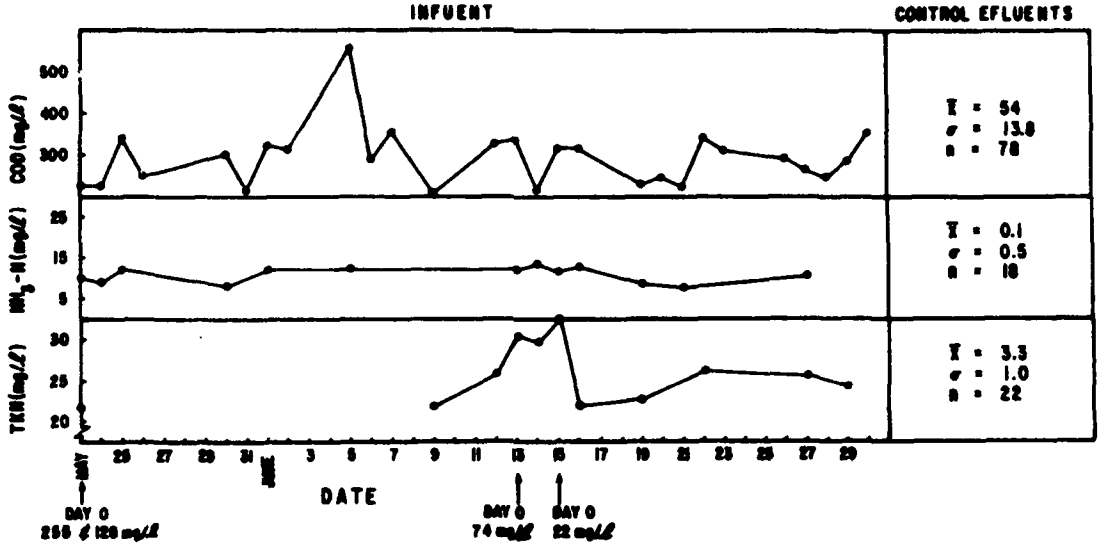


Figure 63. Influent and Control Effluent COD and Nitrogen Data During the Slug UDMH Recovery Periods

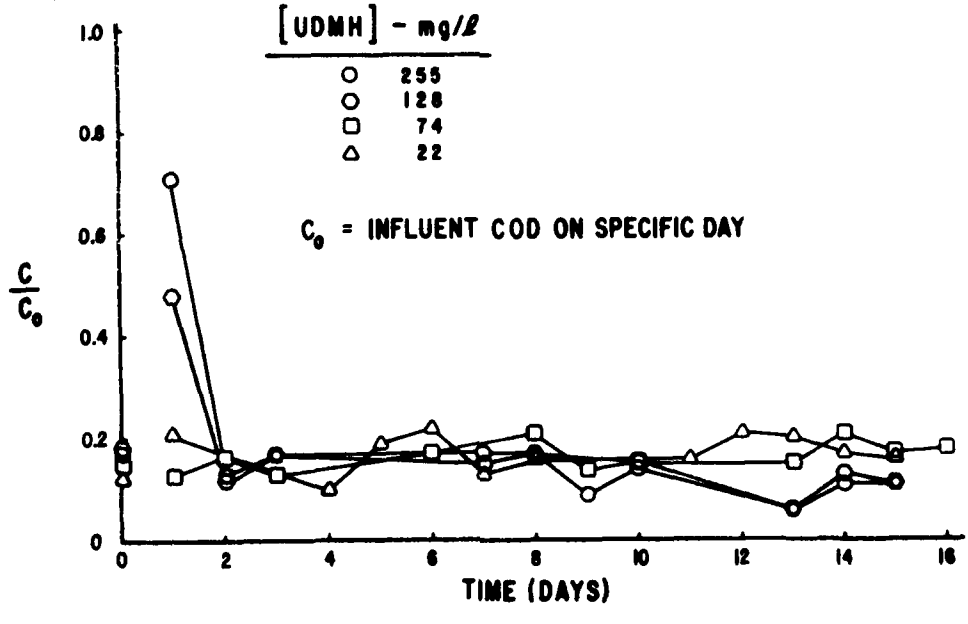


Figure 64. Effluent COD Recovery Following Slug UDMH Loads (Mean of Duplicates)

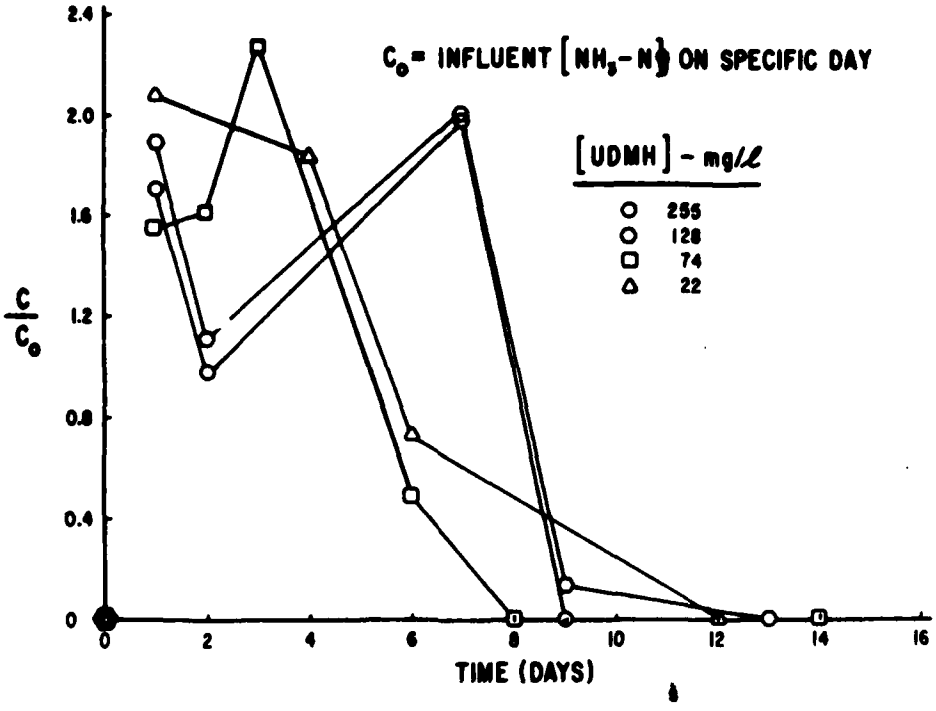


Figure 65. Effluent Ammonia Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates).

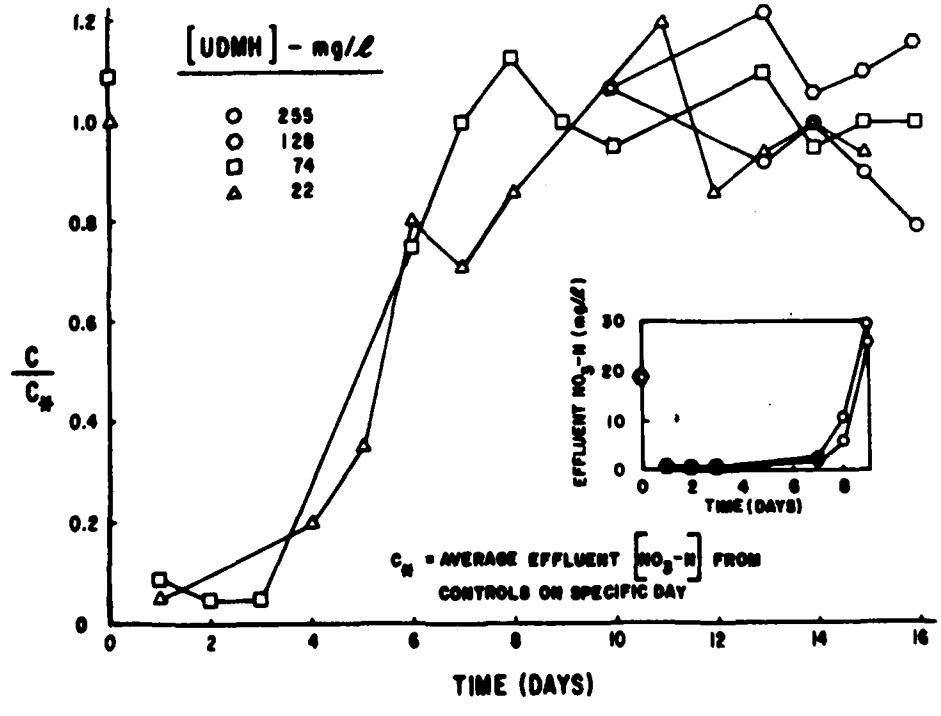


Figure 66. Effluent Nitrate Nitrogen Recovery Following Slug UDMH Loads (Mean of Duplicates)

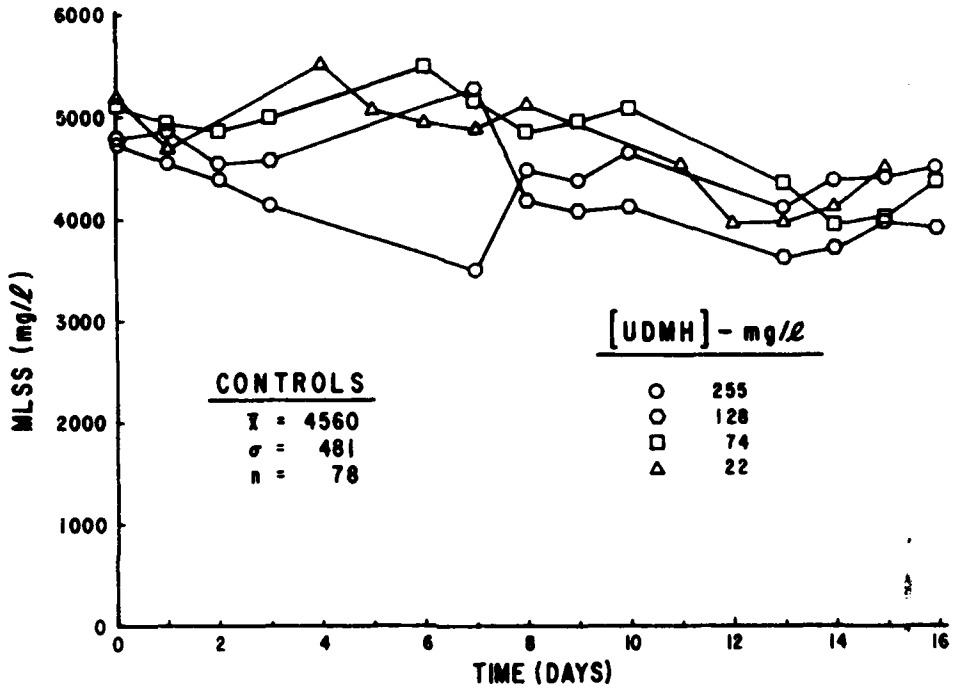


Figure 67. MLSS Response to Slug UDMH Loads as a Function of Time (Mean of Duplicates)

SECTION VII

SUMMARY

1. CONTINUOUS FEED STUDIES

It is apparent from the continuous feed studies that the three hydrazines could cause significant deterioration of an activated sludge plant if the concentration in the influent exceeded a few mg/ℓ. For a reactor with hydraulic detention time (θ) of 9 hours and solids recycle ($\theta_c \sim 7$ days), the efficiency of organic carbon removal as measured by COD is seriously degraded when the influent concentration of hydrazine exceeds 10 mg/ℓ. For UDMH and MMH, total failure is caused by concentrations of approximately 8 mg/ℓ and 5 mg/ℓ, respectively. In contrast to hydrazine and MMH, it appears that after 2 days the heterotrophic organisms begin to acclimate even to the ~20 mg/ℓ UDMH feed concentration. Unfortunately, this test was terminated after 4 days so this conclusion should be made cautiously. Interpolating for the continuous feed studies reported here, the no effect level would be approximately 2 mg/ℓ for hydrazine and 1 mg/ℓ for MMH and UDMH.

Even if sufficient control could be maintained to insure dilution to these levels, complete degradation of the influent hydrazine would not be achieved. Only at the lowest hydrazine concentrations tested (< 1 mg/ℓ) was the effluent feed concentration below detection limits. For MMH and UDMH, the maximum removal efficiency observed was 89 percent and 96 percent, respectively. Studies on the effect of these fuels on algae have established no effect concentrations of less than 0.001 mg/ℓ for MMH and 1.56 mg/ℓ for UDMH (Reference 24). To maintain these low effluent concentrations would require restricting influent concentrations to below 1 mg/ℓ for the three fuels.

The influence of the hydrazines on nitrogen speciation is more pronounced than that found for carbon oxidation. Other nitrogen compounds shown to be powerful selective inhibitors of nitrification include thiourea, thioacetamide dithio-oxamide and cyanide. Inhibition of nitrification occurred at concentrations above 0.5 mg/ℓ for MMH and 1 mg/ℓ for the other fuels. These concentrations are significantly lower than the 10^{-3} M (32 mg/ ℓ) concentrations found by Yoshida and Alexander Reference 17) to inhibit Nitrosomanos. Indeed, they stated that ammonia oxidation still proceeded in the presence of 10^{-2} M(320 mg/ℓ) hydrazine. This was indirectly inferred from data on the formation of hydroxylamine which could result from some other mechanism rather than ammonia oxidation. This selective effect could not be observed for hydrazine and MMH in the studies reported here. Both organisms appeared to be equally effected by comparison of the ammonia oxidation and nitrate formation data in Figure 13 and 15 and Figures 33 and 35. From Figures 53 and 55 it is possible to infer a less immediate effect on ammonia oxidation than nitrate formation; however, in the operation of an activated sludge plant, such information is of minor importance. The results shown in Figure 13 illustrate that in this study ammonia oxidation ceased or was severely reduced at hydrazine concentrations greater than 1 mg/ℓ as reflected in increasing ammonia and decreasing nitrate concentrations in the reactor effluents. Maintaining a stable organic nitrogen concentration

proved difficult and so quantitative evaluation of the effect of the fuels on effluent ORG-N is difficult to ascertain. Qualitatively, removal of organic nitrogen closely parallels removal of COD. This is particularly evident in the UDMH studies which exhibit a much lesser disruption even at 20 mg/ℓ, although from data on degradation of the three fuels (Tables 9, 15, and 21) the reduced toxicity cannot be attributed to lower equilibrium UDMH concentrations in the reactors. UDMH displayed the highest stability to degradation with an average reactor concentration of 12.6 mg/ℓ compared to 6.1 mg/ℓ for hydrazine and 3.7 mg/ℓ for MMH for a nominal feed concentration of 20 mg/ℓ. The percentage fuel degradation in the reactors can be estimated from the decay constants determined in the spill studies. Using a mass balance on the completely mixed flow reactor (CMFR) and assuming steady state conditions, the ratio of effluent concentrations to influent concentration can be calculated:

$$\frac{C}{C_o} = \frac{1}{1 + K\Theta} \qquad (26)$$

The percentage removals were calculated using a hydraulic detention time (Θ) of 6.67 hours and the decay constants for the fuels at the lowest slug concentration, nominally 25 mg/ℓ. The steady state percentage reductions (77 percent for hydrazine, 67 percent for MMH, and 39 percent for UDMH) compare favorably with the measured levels except for MMH. The low degradation of UDMH and the corresponding reduced toxicity implies that UDMH is taken up less by the heterotrophs and autotrophs than both hydrazine and MMH.

The impact on nitrification again reflects the correlation between percentage degradation of the fuel and toxicity. The reason for MMH displaying a more toxic effect to autotrophs than hydrazine is not apparent. This is the opposite trend shown in algae and fish batch studies. These studies, however, are biased by the different degradation rates of the fuels (References 23 and 24).

Mixed liquor suspended solids (MLSS) were relatively stable for all the experiments even though the reactors had quit functioning. It must be assumed that non-viable cells are a major portion of the remaining sludge.

2. SLUG FEED STUDIES

Although continuous addition of hydrazine to the sanitary sewage system is not recommended, it is important to know the effect of one time fuel doses on a treatment plant. Slug loads could result from an accidental spill that reaches the sanitary sewer system or the disposal of an improperly neutralized waste solution. Because of the short exposure, the effect of transient high concentrations of fuel would be expected to be less than a continuous exposure. Figures 17, 37, and 57 show the concentrations of hydrazines expected from strictly hydraulic decay (dilution) in a completely mixed flow reactor (CMFR) and the measured concentrations. It is apparent that there is uptake or breakdown of the fuel which is not experienced in the absence of the biological solids.

TABLE 27. GALLON EQUIVALENTS OF FUEL WHICH WILL PRODUCE AERATION BASIN CONCENTRATIONS OF INTEREST (1, 5, 25, 250 mg/ℓ) DURING SPILL SITUATIONS FOR VARIOUS HYDRAULIC DETENTION TIMES AND FLOW RATES

	HYDRAULIC DETENTION TIME, Θ															
	4 HOURS				8 HOURS				12 HOURS				9 DAYS			
FLOW	1	5	25	250	1	5	25	250	1	5	25	250	1	5	25	250
50,000 GPD	0.008	0.04	0.21	2.1	0.016	0.08	0.4	4	0.024	0.12	0.6	6	0.43	2.2	10.8	108
100,000 GPD	0.016	0.08	0.4	4	0.032	0.16	0.8	8	0.048	0.24	1.2	12	0.86	4.3	21.5	215
200,000 GPD	0.032	0.16	0.8	8	0.064	0.32	1.6	16	0.096	0.48	2.4	24	1.73	8.7	43.3	433
500,000 GPD	0.08	0.4	2	20	0.16	0.8	4	40	0.24	1.2	6	60	4.32	21.6	108	1080
1 MGD	0.16	0.8	4	40	0.32	1.6	8	80	0.48	2.4	12	120	8.64	43.2	216	2160
2 MGD	0.32	1.6	8	80	0.64	3.2	16	160	0.96	4.8	24	240	17.3	86.4	432	4320
10 MGD	1.6	8	40	400	3.2	16	80	800	4.8	24	120	1200	86.4	432	2160	21600
20 MGD	3.2	16	80	800	6.4	32	160	1600	9.6	48	240	2400	173	864	4320	43200
50 MGD	8	40	200	2000	16	80	400	4000	24	120	600	6000	432	2160	10800	108000

NOTE: Volumes of fuel were calculated based on a density of 1.00 gm/ml (i.e. HZ). These values will be conservative for MMH and UDMH. The appropriate multiplication factors are:

MMH : 1.14
UDMH: 1.27

These bacterial decay constants are given in Tables 13, 19, and 25. The use of the term constant is a misnomer since, as shown for each fuel, the rate constant decreases with increasing fuel concentrations. Even though a simple first order reaction was assumed, this may not be the case and some complex reaction may be required to account for the disappearance of the fuel at a molecular level. The additional decay of the fuels observed in the reactors could be due to catalysis of the oxidation due to metals released from the stressed and lyzed cells; however, without more rigorous experiments, it is not possible to speculate on a mechanism. It is important to note that if a spill is large enough to produce the concentrations studied here (25 to 250 mg/ℓ) fuel will still remain in the plant effluent. Even for the lowest concentration used, ∿25 mg/ℓ, the effluent still contained hydrazine concentrations well above those found toxic to fish, algae, and other aquatic organisms.

Table 27 outlines the quantity of fuel required to produce concentrations from 1 to 250 mg/ℓ for different size reactors (sewage treatment plant aeration basins). For a (1 MGD) plant with a hydraulic detention time of ∿8 hours, typical of some AF installations, a 24.6-liter (6.5-gallon) spill from a F-16 emergency power unit would create a concentration of 14 mg/ℓ in a completely mixed aeration basin. Since the basin is completely mixed, the immediate effluent concentration would also be 14 mg/ℓ. In contrast to the continuous feed situation, however, an acute dose of this magnitude produces a minimal effect on plant operation. Figures 19, 39, and 59 present data on the influence of acute doses up to 273 mg/ℓ on COD removal. The concentration which causes no significant effect is 74 mg/ℓ for UDMH, 44 mg/ℓ for hydrazine, and ∿32 mg/ℓ for MMH. Since both MMH and UDMH contribute COD, this must be accounted for to realistically compare the removal of COD from the substrate feed. For instance, 2 hours following a 225-mg/ℓ UDMH slug, 295 mg/ℓ of the 347 mg/ℓ measured COD can be attributed to the fuel itself. Using semibatch reactor kinetics, it is possible to calculate the effluent COD given the influent COD, initial reactor COD, and the COD of the specific fuel using Equation (27).

$$COD_{EFF} = COD_{INIT} \quad - \frac{1}{\theta} t + COD_{INF} \left(1 - \quad - \frac{1}{\theta} t \right) \qquad (27)$$

Comparing calculated effluent COD with measured COD in Figure 68 reveals a significant difference at the first hour. Measured CODs are only ∿ 60 percent of the calculated value. For longer times, the calculated and measured values are remarkably close. The discrepancy at the short reaction times may be due to poor circulation between the clarifier and reactor. This same trend is apparent for effluent ammonia concentration, as shown in Figure 69. Figures 24, 44, and 64 illustrate that, for single exposures, COD removal returns to normal after 7 days for hydrazine and only 2 days for MMH and UDMH.

As in the continuous feed studies, the influence of slug fuel doses on the autotrophic organism is much more significant than on the heterotrophs. Ammonia oxidation is effected for all three fuels at the lowest concentrations tested. The decrease in nitrate exhibited by reactors dosed with hydrazine and UDMH is slightly slower than would be expected from simple wash-out from the reactor. The rapid decrease seen with MMH is unexplained.

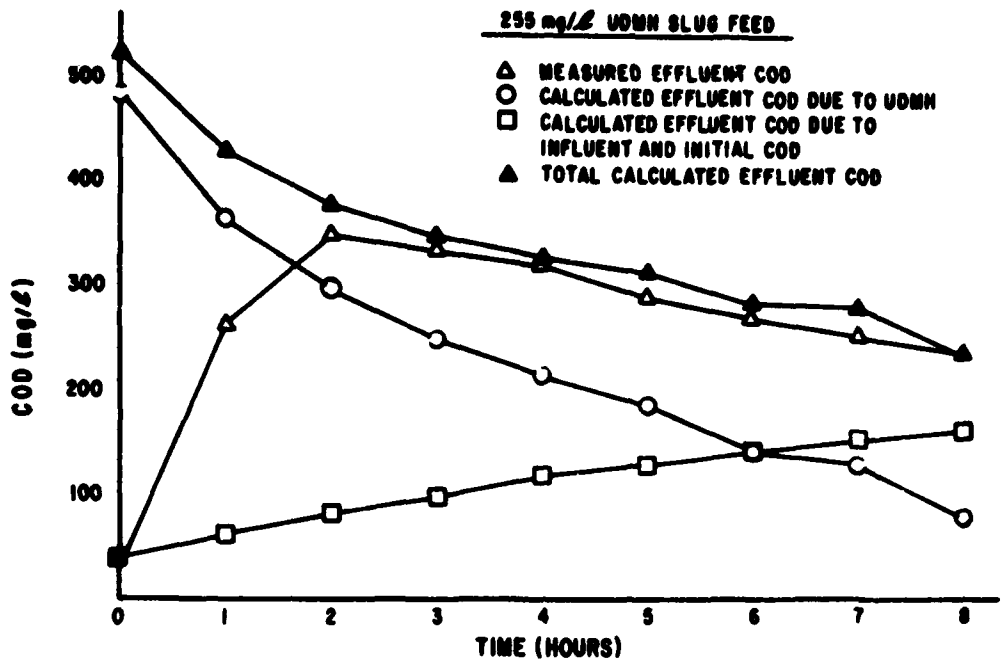


Figure 68. COD Mass Balance for Slug UDMH Load

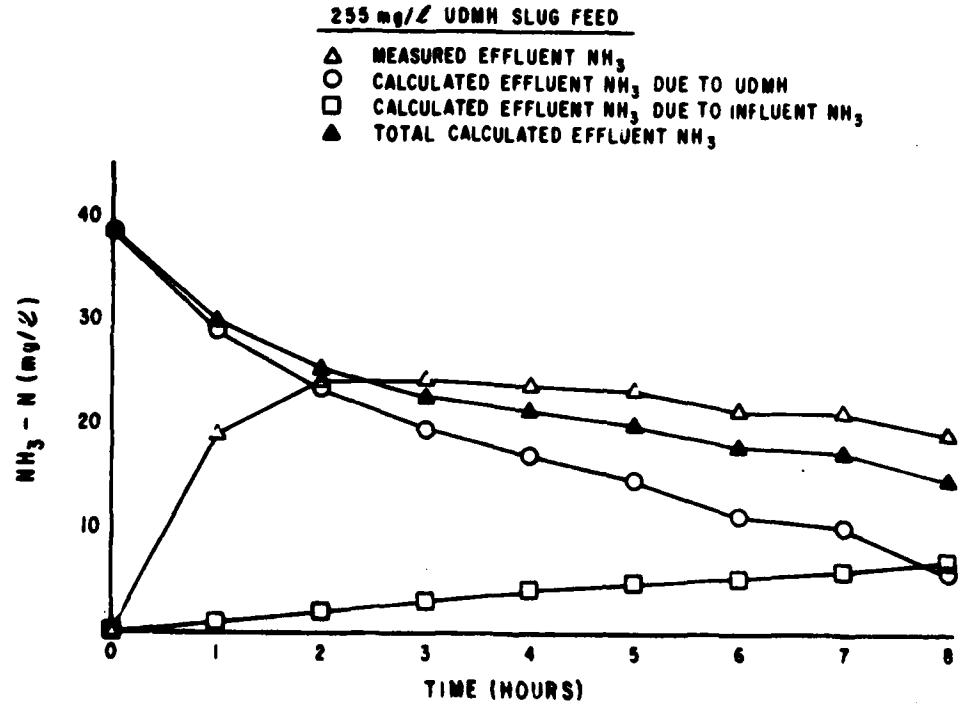


Figure 69. NH_3 Mass Balance for Slug UDMH Load

Attempts to document a reaction between MMH and NO_3^- or an interference with the nitrate probe were negative; nor is it likely that anaerobic denitrification could explain the rapid decrease seen for all 4 initial concentrations studied. A possible explanation might be that,under the conditions existing in the reactors,a catalyzed reaction between MMH and NO_3^- occurred. Unfortunately this was not evaluated while the reactors were operating.

SECTION VIII

CONCLUSIONS

Continuous Feed-All Fuels

- The use of activated sludge for continuous treatment of waste hydrazine fuel is not recommended. The rigid controls required to insure influent concentrations are maintained below the no effect level (1 mg/ℓ) would not be practical.

- Discharges from pretreatment processes must be held to concentrations low enough to prevent values greater than 1 mg/ℓ in the influent to Privately Owned Treatment Works (POTW) using activated sludge treatment to insure they are not adversely affected and that final fuel discharges into receiving waters are below environmentally significant levels.

Slug Loads-HZ

- Treatment plant efficiency, as measured by COD removal, is not seriously impaired for slug doses which result in aeration basin fuel concentrations up to 44 mg/ℓ.

- COD recovery times for slug doses up to 243 mg/ℓ are on the order of 4 to 5 days.

- Nitrification ceased at slug doses above 23 mg/ℓ. The no effect concentration with respect to ammonia oxidation is between 1 to 23 mg/ℓ.

- Ammonia recovery times for slug doses up to 243 mg/ℓ are on the order of 7 to 10 days.

Slug Loads-MMH

- Treatment plant efficiency, as measured by COD removal, is not seriously impaired for slug doses which result in aeration basin MMH concentrations up to 32 mg/ℓ.

- COD recovery times for slug doses up to 273 mg/ℓ are on the order of 2 to 3 days.

- Nitrification ceased at slug doses above 32 mg/ℓ. The no effect concentration with respect to ammonia oxidation is between 1 to 32 mg/ℓ.

- Ammonia recovery times for slug doses up to 273 mg/ℓ are on the order of 12 to 16 days.

Slug Loads-UDMH

- Treatment plant efficiency, as measured by COD removal, is not seriously impaired for slug doses which result in aeration basin UDMH concentrations up to 74 mg/ℓ.

- COD recovery times for slug doses up to 255 mg/ℓ are on the order of 2 to 3 days.

- Nitrification ceased at slug doses above 32 mg/ℓ. The no effect concentration with respect to ammonia oxidation is between 1 to 22 mg/ℓ.

- Ammonia recovery times for slug doses up to 255 mg/ℓ are on the order of 8 to 12 days.

(The reverse of this page is blank)

REFERENCES

1. Sherrard, J. H., "Kinetics and Stoichiometry of Completely Mixed Activated Sludge", Journal Water Pollution Control Fed., Sep 1977.

2. Piel, K.M., and A. F. Gaudy, Jr, "Kinetic Constants for Aerobic Growth of Microbial Populations Selected with Various Single Compounds and with Municipal Wastes as Substrates", Applied Microbiology, 21, 253-256, 1971.

3. Eckhoff, D. W., and D. Jenkins, "Activated Sludge Systems, Kinetics of the Steady and Transient States", Report No. 67-12 of the Sanitary Engineering Research Laboratory, University of California, Berkley, 1967.

4. Metcalf and Eddy, Wastewater Engineering, McGraw-Hill Book Co., New York, New York 1972.

5. Lawrence, A. L. and P. L. McCarty, "A Unified Basis for Biological Treatment Design and Operation", Journal of the Sanitary Engineering Division, ASCE, 96, 1970.

6. McCarty, P. L., "Stoichiometry of Biological Reactions." Paper presented at the International Conference, "Toward a Unified Concept of Biological Waste Treatment Design," Atlanta, Georgia (October 6, 1974).

7. Stanill, Roger Y., The Microbial World, 4th Edition, Prentice-Hall Inc., Englewood Cliffs, NJ, 1976.

8. Hoover, S. R., and Porges, N., "Assimilation of Dairy Wastes by Activated Sludge II, The Equation of Synthesis and Oxygen Utilization." Sewage and Industrial Wastes, 24 306 (1952).

9. McCarty, P. C., "Phosphorous and Nitrogen Removal by Biological Systems", presented at 2nd Sanitary Engineering Research Laboratory Workshop, Tahoe City, California, June 26, 1970.

10. Wild, H. E., Sawyer and McMahon, "Factors Affecting Nitrification Kinetics," JWPCF, 43, 1971.

11. Stratton, Frank E., and P. L. McCarty, "Prediction of Nitrification Effects on the Dissolved Oxygen Balance of Streams", Environmental Science and Technology, (5) May 67.

12. Monod, J., "La Technique of Culture Continue; Theorie et Applications," Annals Institute Pasteur, Vol. 79, 1950.

13. Heukelekian, H., Orford and Manganelli, "Factors Affecting the Quantity of Sludge Production in the Activated Sludge Process," Sewage and Industrial Wastes, Vol. 23, No. 8, August 1951.

14. Christensen, Douglas R. and P. L. McCarty, "Biotreat: A Multi-Process Biological Treatment Model", Presented at the Annual WPCF Conference, Denver, Colorado, October 1974.

15. Tomlinson, T. G., et al, "Inhibition of Nitrification in the Activated Sludge Process of Sewage Disposal," Journal Applied Bacteriology, 29, 266, 1966.

16. Meyerhof, O., "Die Atmung des Nitritbildners und ihre Beeinflussung durch chemische Substanzen," Pflugers Arch. ges. Physiol. 166, 240.

17. Yoshida, T. and Alexander, "Hydroxylamine Fourmation by Nitrosomonas Europala", Canadian Journal of Microbiology, Vol. 10, 1964.

18. Water Pollution Control Fed., Wastewater Treatment Plant Design; Manual of Practice No. 8, WPCF, Washington, DC, 1977.

19. Watt, George W. and Chrisp, "A Spectrophotometric Method for the Determination of Hydrazine," Analytical Chemistry, Vol. 24, No. 12, December, 1952.

20. Pinkerton, M. K., et al, "A Colorimetric Determination for 1,1-Dimethylhydrazine (UDMH) in Air, Blood and Water," American Industrial Hygiene Association Journal, Vol. 24, May-June 1963.

21. Verotrack, W. and M. Alexander, "Heterotrophic Nitrification by Arthrobacter sp," Journal of Bacteriology, June 1972.

22. Saleh, M.M. and A. F. Gaudy, Jr., "Shock Load Response of Activated Sludge with Constant Recycle Sludge Concentration," Journal Water Pollution Control Fed., April 1978.

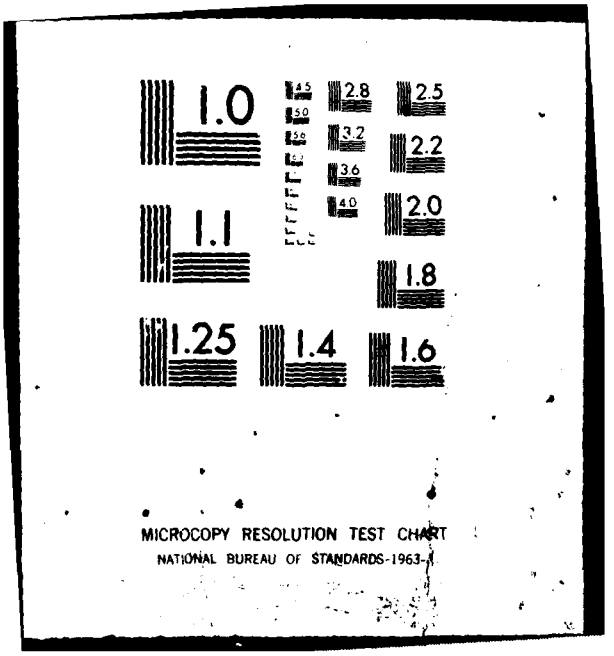
23. Klein, S. A., and D. Jenkins, "Environmental Quality Research. Fish and Aufwuchs Bioassay. Third Annual Report" AMRL-TR-78-65, Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio, November 1978.

24. Scherfig, J., P. S. Dixon, and C. A. Justice, "Environmental Quality Research, Use of Unicellular Algae for Evaluation of Potential Aquatic Contaminants, Third Annual Report". AMRL-TR-78-86, Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, November 1978.

AD-A085 186 AIR FORCE ENGINEERING AND SERVICES CENTER TYNDALL AF--ETC F/G 21/9.1
THE EFFECTS OF AMINE-BASED MISSILE FUELS ON THE ACTIVATED SLUDG--ETC(U)
OCT 79 M G MACNAUGHTON, J A FARMWALD

UNCLASSIFIED AFESC/ESL-TR-79-39 NL

END
DATE FILMED
6-80
DTIC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

APPENDIX A

STOICHIOMETRY

A. General: The stoichiometric relationship developed by McCarty (Reference 6) is as follows:

$$R = R_d - f_e R_a - f_s R_c \qquad \text{(A-1)}$$

R = overall reaction

R_d = half reaction for electron donor

R_a = half reaction for electron acceptor

R_c = half reaction for cell synthesis

f_e = fraction of e^- donor used for energy

f_s = fraction of e^- donor used for synthesis

where: $f_e + f_s = 1$.

In suspended growth systems, f_e and f_s are a function of cellular yield and the organism decay rate, the latter being a function of solids retention time. Using the classical growth equation for microorganisms and mass balance relationships for a suspended growth system, McCarty developed the following relationship:

$$f_s = a_e \left(1 - \frac{f_d\, b\, \Theta_c}{1+b\ \Theta_c}\right) \qquad \text{(A-2)}$$

where: a_e = cell yield coefficient expressed as equivalents of cells per equivalent of donor consumed (Figure A-1). a_e and b can be estimated from kinetic studies for a particular waste or from thermodynamic considerations. Oftentimes values are assumed based on previous work with similar wastes. The fraction f_d is most often assumed to be 0.8 for both aerobic and anaerobic organisms (Reference 1). Thermodynamic relationships, as reported by McCarty (Reference 6), are given by Equations (A-3) and (A-4).

$$a_e = \frac{1}{1 + A} \qquad \text{(A-3)}$$

$$A = -\frac{\Delta G_p/k^m + \Delta G_n/k + 7.5}{k\Delta G_r} \qquad \text{(A-4)}$$

ΔG_p = energy required to convert cell carbon source to an intermediate stage

$= \Delta G^o(w)_d + 8.54$

= 27.22 Kcal for inorganic e^- donors

$\Delta G^o(w)d$ = free energy per mole of electrons for donor half reaction.

m = +1 if ΔG_p is >0, -1 if <0

$\Delta G_r = \Delta G^o(w)_d - \Delta G^o(w)_a$

$\Delta G^o(w)_a$ = free energy per mole of electrons for acceptor half reaction.

k = efficiency of energy transfer for bacterial growth, ranging from 0.4 - 0.7.

ΔG_n = energy required to convert the nitrogen source for cell synthesis to NH_3.

B. Heterotrophic Reactions: Using the data presented in Tables 1 and 2 and McCarty's procedure for constructing empirical formulations based on electron equivalent fractions of each component in the waste (Appendix B), the following relationship was developed for the enriched primary effluent and has been taken to represent the heterotrophic donor half reaction, R_d. The balanced equation has been normalized to 1 electron equivalent:

(A-5)

$$0.00398C_{54}H_{96}O_{20}N_7 + 0.35060\ H_2O = 0.21514CO_2 + 0.02789NH_4^+ + 0.97211H^+ + e^-$$

* $\Delta G^o(w) = -7.9$ Kcal/e^- equivalent

The electron acceptor is oxygen; thus R_a is:

$$0.5\ H_2O = 0.25O_2 + H^+ + e^- \qquad \text{(A-6)}$$

*$\Delta G^o(w) = 18.675$ Kcal/e^- equivalent

Assuming an empirical formula for aerobic bacterial protoplasm (Reference 8) and noting that ammonia serves as the nitrogen source, R_c becomes:

$$0.05C_5H_7O_2N + 0.45H_2O = 0.2CO_2 + 0.05HCO_3^- + 0.05NH_4^+ + H^+ + e^- \qquad \text{(A-7)}$$

C. Autotrophic Reactions: The following half reaction applies when NH_4^+ serves as the electron donor.

$$0.125\ NH_4^+ + 0.375\ H_2O = 0.125\ NO_3^- - 1.25\ H^+ + e^- \qquad \text{(A-8)}$$

$\Delta G^o(w) = 8.245$

The reactions R_a and R_c are the same as for the heterotrophic situation.

*Reactants and products at unit activity except $H^+ = 10^{-7}$

D. Yield Coefficients: The bacterial yield coefficient, Y, expressed as grams cells/gram substrate removed may be estimated by writing the overall reaction, R, for the condition $\Theta_c = 0$ (reference Figure A-1). The substrate of interest in the autotrophic reaction is NH_4^+-N which is amenable to direct measurement. However, since this is not the case for the heterotrophic substrate, it becomes advantageous to develop a relationship between organic substrate concentration and a standard parameter such as COD.

1. COD: The theoretical chemical oxygen demand for the supplemented feed solution may be calculated from the empirical formulation, thus:

$$C_{54}H_{96}O_{20}N_7 + 62.75O_2 \rightarrow 54CO_2 + 37.5\ H_2O + 7\ NH_3 \qquad \text{(A-9)}$$

On a molar basis, 1 mole donor ≡ 2008 gm COD. Based on a total organic fraction of 223 mg/ℓ in the enriched feed (118.7 mg carbohydrate + 37.3 mg protein + 16.9 mg fat + 50 mg 1^o effluent (measured value), a value of 433 mg/ℓ COD results. Actual analyses of the primary effluent yielded 100 mg COD/50 mg yss/ℓ which is, in fact, equal to the value predicted from the empirical formula $C_{10}H_{19}O_3N$ used in constructing the donor half reaction. The composite Slender® formulation, $C_{42}H_{71}O_{16}N_6$, does, however, yield a value 29 percent higher (286,000 mg/ℓ) than that determined experimentally.

2. Heterotrophic Y: Assuming a k value of 0.6 (Reference 6) and employing $\Delta G^o(w)$ values developed in paragraph B, Equations (A-3) and (A-4) are used to find that $a_e = 0.65$. If $f_d = 0.8$, it follows from Equation (A-2) that $f_s = a_e$ and therefore $f_e = 0.35$. Substituting into Equation (A-1) yields the following relationship for R.

(A-10)

$$C_{54}H_{96}O_{20}N_7 + 8.17HCO_3^- + 22O_2 + 1.2NH_4^+ = 8.17C_5H_7O_2N + 29.5H_2O + 21.4CO_2$$

From the above coefficients and those relationships derived from equation (A-9) Y is 0.46 gm cells/gm COD removed. This value compares well with values reported in the literature for similar wastes (Reference 5).

3. Autotrophic Y: Again a_e may be calculated from thermodynamic considerations assuming k = 0.6. Thus, when $\Theta_c = 0$; $a_e = 0.11$, $f_s = 0.11$, and $f_e = 0.89$.

The overall autotrophic reaction is constructed and used to estimate Y on a gram cells/gram NH_4^+-N removed basis.

(A-11)

$$0.1305NH_4^+ + 0.225O_2 + 0.022CO_2 + 0.0055HCO_3^- = 0.0055C_5H_7O_2N + 0.125\ NO_3^- + 0.1195\ H_2O + 0.25\ H^+$$

$$Y = 0.34 \text{ gm cells/gm } NH_4^+ \text{-N}$$

E. Supplemental Requirements: As discussed in paragraph A, f_e, f_s, and hence R, under actual operating conditions, are a function of b, f_d, and θ_c. By writing balanced Stoichiometric reactions as a function of θ_c (constant b, f_d), it can be shown that oxygen and alkalinity demands increase with increasing cell residence times. The advantages of approaching such an extended aeration system are lower observed yields ($Y_{OBS} = Y/1+b\ \theta_c$), effluent soluble substrate concentrations, and nutrient requirements.

1. Nutrients: In the interest of making conservative estimates the worst case was considered for the desired influent substrate concentrations, i.e., maximum yield ($\theta_c = 0$) and complete substrate utilization ($S^e = 0$). The assumption indicates that Equations (A-10) and (A-12) should be used to estimate maximum yield nitrogen and phosphorous requirements.

a. Nitrogen:

(1) Heterotrophic: Using the appropriate stoichiometric Equation (A-10), it is clear that one mole of donor requires 1.2 moles of NH_4^+-N for complete oxidation to occur. Based on an influent donor mass of 223 mg/ℓ (organic fraction), it can be shown that a nitrogen requirement of 3.2 mg/ℓ exists, the theoretical organic nitrogen supplied by the donor being 160 mg/ℓ. Note that rule-of-thumb estimates are often made, based on the same yield and utilization assumptions employed here, assuming the typical aerobic cell contains 12-percent nitrogen. In this case, the resultant 17.6 mg/ℓ value compares well with the stoichiometric total of 19.2 mg/ℓ. Referring to Table 1, it is seen that approximately 12.7 mg/ℓ of inorganic nitrogen is present in the raw feed solution. While this should provide an adequate excess of nitrogen, an additional 4.7 mg/ℓ urea-N was routinely added to insure nitrogen was not limiting.

(2) Autotrophic: Considering all sources, the total organic and inorganic nitrogen in the described system is approximately 33.4 mg/ℓ*. Of this, 19.2 mg/ℓ is required for heterotrophic synthesis, the remainder, 14.2 mg/ℓ, being available for nitrification. This total value agrees well with the average Kjeldahl nitrogen (29.8 mg/ℓ) in the supplemented feed which was monitored throughout the study.

b. Phosphorous: As stated earlier, the phosphorous requirement is generally considered to be about 1/5 that of nitrogen. This rule of thumb assumes the typical aerobic cell contains approximately 2-percent phosphorous. In lieu of stoichiometry which includes a phosphorous component, this information, again based on maximum yield and complete substrate utilization, may be used to estimate the phosphorous demands.

* 1^o Effluent inorganic-N: 12.7 mg/ℓ
Electron donor organic-N: 16.0 mg/ℓ; based on empirical formulation.
Supplemental organic-N: 4.7 mg/ℓ UREA-N

(1) Heterotrophic: Using a yield coefficient of 0.46 and an influent substrate concentration of 320 mg/ℓ as COD, the resultant phosphorous requirement is 2.9 mg/ℓ.

(2) Autotrophic: The autotrophic demand for phosphorous is expected to be low. Using the appropriate values, the calculations indicate a demand of 0.10 mg/ℓ-P.

2. Oxygen and alkalinity: Conservative estimates of oxygen and alkalinity requirements were made based on a mean cell residence time of 20 days. The apppropriate stoichiometry is summarized below.

HETEROTHROPHIC: $a_e = 0.65$ $f_s = 0.39$, $f_e = 0.61$

$$C_{54}H_{96}O_{20}N_7 = 7H^+ + 38.3O_2 + 4.9HCO_3^- \rightarrow 4.9C_5H_7O_2N + 34.5CO_2 + 32.6\ H_2O + 2.1NH_4^+ \quad \text{(A-12)}$$

AUTOTROPHIC: $a_e = 0.11$ $f_s = 0.066$, $f_e = 0.934$

$$NH_4^+ + 0.103CO_2 + 1.82\ O_2 + 0.026\ HCO_3^- \rightarrow 0.026C_5H_7O_2N + 0.974NO_3^- + 1.95H^+ + 0.949\ H_2O \quad \text{(A-13)}$$

The above relationships lead to the requirements outlined in Table A-1, assuming complete substrate utilization.

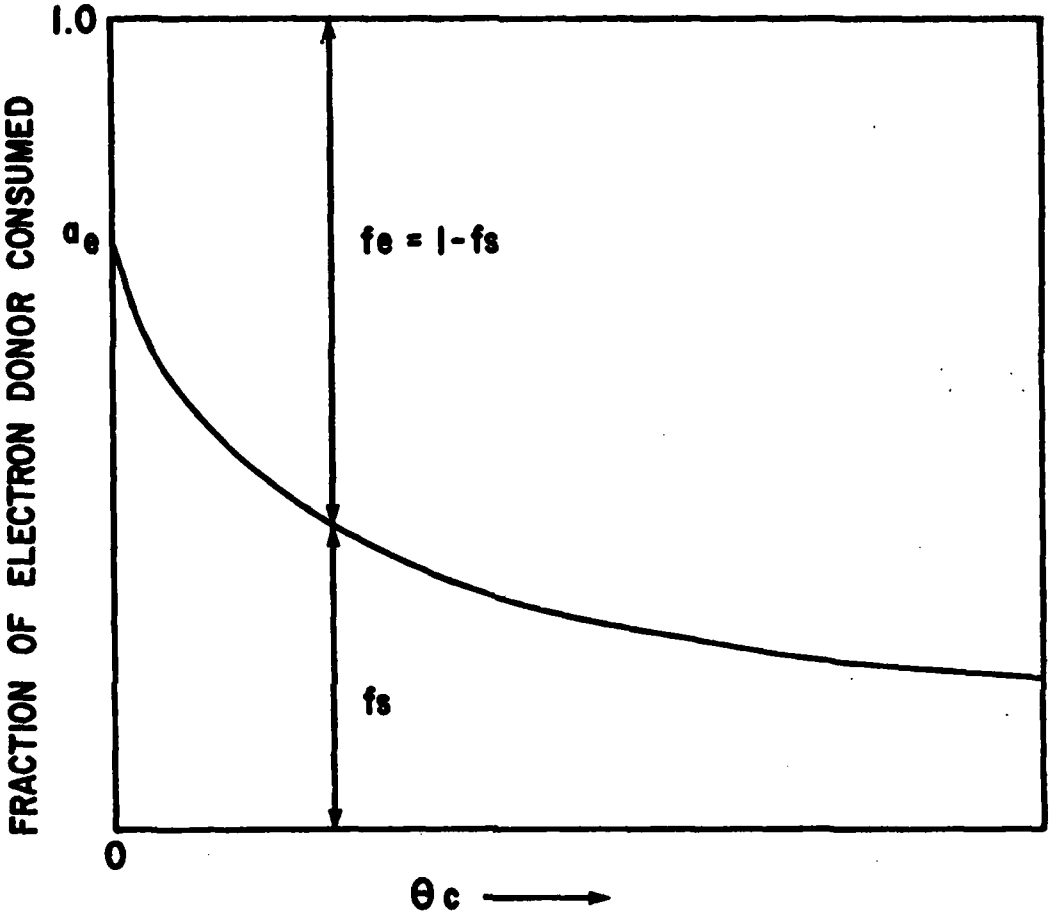


Figure A-1. Fraction of Electron Donor Used for Energy, f_e, and for Synthesis, f_s, as a Function of θ_c. A_e is the Maximum Cell Yield Coefficient on an Equivalent Basis

TABLE A-1. OXYGEN AND ALKALINITY REQUIREMENTS θ_c = 20 DAYS

	Design S^o	O_2 gm/DAY	Alkalinity mg/ℓ as $CaCO_3$
Heterotrophic	320 mg/ℓ COD	4.20	2260*
Autotrophic	15 mg/ℓ NH_4-N	1.35	150**
Total		5.55	2410

* Based on Carbonic Acid Equilibria, pH $\geq$ 7.0 (Appendix C) and HCO_3^- requirements for synthesis.

** Assumed 10 times the NH_4^+ -N to be oxidized (Reference 9).

APPENDIX B

EMPIRICAL FORMULATIONS

Raw Feed

1^{o} EFF (Domestic Sewage) 1/50 $C_{10}H_{19}O_3N$

50 mg/ℓ vss (measured value)

$$(0.05\ gm)\ \frac{mole}{201gm} = 0.0002488\ Mole\ \frac{50\ eq}{Mole} = \underline{0.0124}\ eq$$

Slender®

Carbohydrate 1/4 CH_2 0.1187 gm/ℓ (Slender® Label)

$$(0.1187\ gm)\ \frac{1\ mole}{14\ gm}\ \frac{4\ eq}{mole} = \underline{0.0339}\ eq$$

Fat 1/46 $C_8H_{16}O$ 0.0169 gm/ℓ (Slender® Label)

$$(0.0169\ gm)\ \frac{1\ mole}{128\ gm}\ \frac{46\ eq}{mole} = \underline{0.00607}\ eq$$

Protein 1/66 $C_{16}H_{24}O_5N_4$ 0.0373 gm/ℓ (Slender® Label)

$$(0.0373\ gm)\ \frac{1\ mole}{352\ gm}\ \frac{66\ eq}{mole} = \underline{0.00699}\ eq$$

Total equivalents = 0.0594

Total Slender equivalents = 0.04696

FRACTIONS ON EQ BASIS

Component	Slender Only®	Enriched Feed
1^{o} EFF	--	0.21
Carbohydrate	0.72	0.57
Protein	0.15	0.12
Fat	0.13	0.10

Enriched Feed Formulation:

$$0.21\ (C_{10}H_{19}O_3N) + 0.57\ (CH_2O) + 0.12\ (C_{16}H_{24}O_5N_y) + 0.1\ (C_8H_{16}O) =$$

$$C_{5.39}\ H_{9.61}\ O_{1.9}N_{0.69} \sim \underline{C_{54}H_{96}O_{20}N_7}$$

$$\Delta G^{O}(w) = \varepsilon\ (\text{Fractions})\ (\text{Component}\ \Delta G^{O}(w))$$

$$\Delta G^{O}(w) = 0.21(-7.6) + 0.57(-10.0) + 0.12(-7.7) + 0.10(-6.6) =$$

$$-7.9\ \text{Kcal/e}^{-}\ \text{equivalent}$$

Similarly Slender Formulation = $\underline{C_{42}H_{71}O_{16}N_6}$

APPENDIX C

CALCULATION OF ALKALINITY REQUIREMENT FOR HETEROTROPHIC REACTION

$$C_{54}H_{96}O_{20}N_7 + 7H^+ + 38.3O_2 + 4.9HCO_3^- \rightarrow 4.9C_5H_7O_2N + 34.5CO_2 + 32.6H_2O + 2.1NH_4^+$$

$$pH = 6.4 + \log \frac{HCO_3}{H_2CO_3^*} \quad pK_1 = 6.4$$

where $H_2CO_3^* = CO_{2\ (aq)} + HCO_3^-$

Assume $H_2CO_3 \ll CO_{2\ (aq)}$ i.e. $H_2CO_3^* \equiv CO_{2\ (aq)}$

Desire pH > 7.0

$$\log \frac{HCO_3^-}{H_2CO_3^*} = \log \frac{HCO_3^-}{CO_{2\ (aq)}} \geq 0.6$$

For each mole of waste 34.5 moles CO_2 produced assume worst case, i.e., all CO_2 becomes $CO_{2\ (aq)}$

$$\log \frac{HCO_3^-}{34.5} \geq 0.6$$

$$\frac{HCO_3^-}{34.5} \geq 3.98$$

$$HCO_3^- \geq 137.3 \text{ moles}$$

In addition: HCO_3^- is destroyed to produce cellular matter, i.e., 4.9 moles per the stoichiometry $HCO_3^- \geq 142$ moles

$$\frac{142 \text{ moles } HCO_3^-}{1 \text{ mole waste}} \quad \frac{1 \text{ mole } C_aCO_3}{1 \text{ mole } HCO_3^-} \quad \frac{100 \text{ gm } C_aCO_3}{1 \text{ mole } C_aCO_3} = 14200 \text{ gm } C_aCO_3/\text{mole waste}$$

$$(320 \text{ mg COD})/\ell \quad \frac{1 \text{ mole waste}}{2008 \text{ gm COD}} \quad \frac{14200 \text{ gm } C_aCO_3}{\text{mole waste}} = 2260 \text{ mg}/\ell \text{ as } C_aCO_3$$

INITIAL DISTRIBUTION LIST

OASD/(I&L)EES	1
OUSDR&E	1
OSAF/MIQ	1
DDC/DDA	2
ARPA	1
OSAF/OI	1
HQ USAF/LEEV	2
HQ USAF/SGES	1
AFMSC/SGPA	1
HQ AFSC/DL	1
HQ AFSC/SD	1
HQ AFSC/DEV	1
HQ AFSC/SGB	1
AMD/RDU	1
AMD/RDB	1
AMRL/THE	1
OEHL/CC	3
USAFSAM/EDE	4
USAFSAM/VNL	1
Strughold Aeromedical Library	1
AFOSR/NL	1
SAMSO/SGX	1
SAMSO/DEV	1
AFRPL/Library	1
AFRPL/LKDP	1
ADTC/DLODL (Tech Library)	1
ASD/AEL	1
FTD/LGM	1
AFWL/SUL (Tech Library)	1
AFTEC/SG	1
HQ SAC/DEPA	1
HQ SAC/SGPA	1
HQ TAC/SGPA	1
HQ TAC/DEEV	1
HQ AFLC/SGP	1
HQ AFLC/DEEPV	2
HQ AFLC/IGYG	1
HQ AFLC/MAXF	1
HQ MAC/SGPE	1
HQ MAC/DEEV	1
HQ ADCOM/SGPAP	1
HQ ADCOM/DEEV	1
HQ ATC/SGPAP	1
HQ ATC/DEEV	1
HQ PACAF/SGPE	1
HQ PACAF/DEEV	1
1 Med Severice Wg/SGB	1
HQ AFISC/SG	2
HQ AAC/SGB	1
HQ AAC/DEEV	1
HQ USAFE/SGB	1
HQ USAFE/DEVS	1
HQ USAFE/DEPV	1
USAF Hospital Weisbaden	1
HQAUL/LSE 71-249	1
HQ USAFA/Library	1
AFIT/Library	1
AFIT/DE	1
AFRES/SGB	1
USAFSS/DEE	1
USAFRCE/DEEV	3
USAFRCE/CR/DEEV	3
USAFRCE/ER/DEEV	3
US Army, MIRADCOM	1
Ch, Environmental Chem Dev/USAEHA	1
USA Med Bioengrg R&D Lab	2
Ch, Industrial Hyg Div USAEHA	2
USA Chief, R&D/EQ	1
USN Chief, R&D/EQ	1
Ch, Pollution Abatement NAVFAC	1
NAPC/Code PE71:AFK	1
NESO	1
US Coast Guard/GDD	1
HQ NASA	1
NCEL	1
NASA/MD-E	1
FAA/AEE-300	1
FAA/ARD-550	1
EPA/ORD	1
Federal Lab Program	1
Library, Chem Abstract Service	1
Toxic Materials Info Ctr	1
HQ AFESC/DEV	4
HQ AFESC/TST	2
HQ AFESC/RDVC	15

(The reverse of this page is blank)